



**THE USE OF ULTRA-VIOLET (UV) LIGHT EMITTING DIODES (LEDs) IN AN
ADVANCED OXIDATION PROCESS (AOP) WITH BRILLIANT BLUE FCF AS**

AN INDICATOR

THESIS

MARCH 2015

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**DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY**

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Robert W. Scott IV, BS

Major, USAF

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Abstract

Water contamination can result from terrorist acts, industrial accidents, or natural phenomena. Advanced Oxidation Processes (AOPs) represent a potentially useful method for water decontamination. This research explored the application of Brilliant Blue FCF as a witness dye in an Advanced Oxidation Process (AOP) employing Ultra-Violet (UV) Light Emitting Diodes (LEDs) with peroxide (H_2O_2). In addition to exploring the attributes of Brilliant Blue FCF within this application, this research employed this dye to evaluate the effect of varied UV LED duty cycles (pulsing) on the reaction rates of a UV/ H_2O_2 AOP. Experiments performed using Brilliant Blue FCF indicated that it performed suitably as a witness dye with improved characteristics as compared to methylene blue. Further, the experiments indicated that when the LEDs were driven at lower duty cycles (e.g., 10 and 5%) they were 165% to 200% more efficient at driving the UV/ H_2O_2 AOP than they were when driven continuously (e.g., a duty cycle of 100%).

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This thesis is only possible due to the contributions of many others not cited in the pages that follow. I am grateful to the God who gave me eyes to see, and ears to hear, and most importantly redeemed my soul. May I use my abilities to do justly, love mercy, and walk humbly with Him (Micah 6:8).

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Robert W. Scott IV

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THE USE OF ULTRA-VIOLET (UV) LIGHT EMITTING DIODES (LEDs) IN AN ADVANCED OXIDATION PROCESS (AOP) WITH BRILLIANT BLUE FCF AS AN INDICATOR

I. Introduction

This chapter describes the problem investigated in this thesis. Specifically, it provides the background of the problem's origin, clearly states the problem, and describes the research and investigative questions. Furthermore, it describes the scope of the research, including assumptions and limitations, briefly describes the methodology used to perform experiments, and provides an overview of the components of the rest of the thesis.

Background

This thesis seeks to build knowledge on the use of Ultra-Violet (UV) Light Emitting Diodes (LEDs) in water decontamination through an Advanced Oxidation Process (AOP). Personnel, vehicles, equipment, and buildings can be contaminated with hazardous chemicals and biological substances through industrial accidents or terrorist acts. Decontamination from such an event often involves large volumes of water (Headquarters Department of the Army 1993). This contaminated wastewater must be treated to degrade the hazardous contaminants to safe levels before it is released into wastewater treatment facilities or the environment. Based on this need for decontamination, the United States Environmental Protection Agency (EPA), National Homeland Security Research Center, Water Infrastructure Protection Division, is sponsoring research on components of the decontamination process. Additionally, the 2014 Quadrennial Defense Review's three-pillar strategy cites military support to civil authorities to mitigate "the effects of potential attacks" as a vital portion of the first pillar,

Protect the Homeland (Department of Defense 2014). Building knowledge of the effective employment of UV LEDs to drive an AOP may prove useful in the future development of decontamination systems. These decontamination systems could be utilized in civilian and military decontamination operations at home and abroad.

The AOP of interest occurs when hydrogen peroxide is added to contaminated water and then exposed to UV light. The UV light decomposes the hydrogen peroxide molecules into hydroxyl radicals, which oxidizes the contaminant into inert or less harmful compounds (Andreozzi, et al. 1999). Currently, the leading source of UV light for this process is mercury-based fluorescent lamps. These lamps are large, fragile, require high voltage and power, and contain mercury, itself a contaminant (Bettles, et al. 2007). UV LEDs are in the early stages of development, but have the potential to drive the AOP and have the advantages of small size, light weight, physical durability, no hazardous components, and they can be powered by low, direct current voltage, which are consistent with portable power sources such as batteries or photovoltaic cells (Crystal IS 2013). Furthermore, it is believed that over time, UV LEDs will be developed which have a long life-cycle similar to their visible spectrum counterparts.

Statement of Problem/Issue

In response to the potential threat of chemical or biological contamination, systems for the decontamination of large quantities of liquid are being investigated by the EPA. UV LEDs are in the early stages of development and have potential for use in future liquid decontamination systems. This research seeks to improve knowledge of viable methods

to efficiently utilize UV LEDs to decontaminate water through an AOP. Understanding of this issue will come through exploration of the research and investigative questions.

Research and Investigative Questions

This study continues work toward addressing the primary research question of: “What operating parameters should be used for the most efficient use of UV LEDs to produce hydroxyl radicals from hydrogen peroxide to drive an AOP?” To guide the thesis research, the following investigative questions were developed:

- 1.) What effect does the tinting from the previously used witness dye (methylene blue) have on the output of the UV LEDs? At the conclusion of experiments conducted by Duckworth (2014), the quartz windows of the UV LEDs used in methylene blue AOP reactions showed noticeable blue staining. This staining may have played a role in generating the non-linear relationship between UV LED duty cycle and dye concentration shown in Duckworth’s data. To understand the possible effect of the methylene blue staining on the preceding data, the effect of staining on light transmission through the UV LED windows must be quantified.
- 2.) What are the characteristics of the EPA recommended replacement witness dye Brilliant Blue FCF (For Coloring Food), also referred to as Brilliant Blue FDC (Food, Drug and Cosmetic or Blue #1, relevant to its use in assessing the performance of an AOP? To generate more accurate experimental results, analysis of the US EPA recommended dye must be performed. This analysis will include a review of literature supporting the use of Brilliant Blue FCF as

a witness dye in AOP experimentation. Determining the dye's behavior in the presence of UV light and H_2O_2 alone will be necessary prior to UV/ H_2O_2 AOP experimentation. Understanding the effects UV light and H_2O_2 exert on Brilliant Blue FCF will aid in accounting for and excluding those effects in experimental design and data analysis. The interactions of Brilliant Blue FCF and the UV LED lenses must be examined to determine if the dye will stain the quartz UV LED windows and affect their ability to transmit UV light. Examining the staining characteristics of Brilliant Blue FCF will aid in controlling for a possible non-linear relationship between duty cycle and hydroxyl radical production in the UV/ H_2O_2 AOP.

- 3.) Are there any UV LED duty cycle (pulsing) routines which could maximize LED power output efficiency (light output/energy input)? To support the effective future employment of UV LEDs, an examination of UV LED characteristics is required. Examining UV LED duty cycles in relation to light output, and more importantly their efficiency in producing hydroxyl radicals in an AOP, is necessary to determine if certain duty cycles produce higher hydroxyl generation efficiencies. Increased understanding of how UV LEDs perform under varied duty cycles may be useful in the use of emerging UV LED technology.
- 4.) What are the effects of differing UV LED duty cycle drive patterns (pulsing) in contrast to continuous (100% duty cycle) UV LED on hydroxyl radical production and the Advanced Oxidation Process (AOP)? The goal of investigating this question is to determine if there is a duty cycle drive pattern

where hydroxyl radical production, and reaction rate for the UV/H₂O₂ AOP, peaks in relation to energy input. Analysis for this question will focus on whether an advantageous non-linear relationship exists between UV LED duty cycle and hydroxyl radical production/AOP reaction rate.

Methodology

The experimentation focused on the investigative questions and involved manipulating current and total exposure time in differing duty cycles. Duty cycle refers to the amount of time the UV LED is on during the experimental period, with a 100% duty cycle being continuously on, and a 30% duty cycle describing a condition where the UV LED is pulsed on and off, being on 30% of the time, and the off the remaining 70%. The experimental trials for this research took place in the AFIT ENV laboratory.

A new witness dye was evaluated for use in these experiments due to the previous dye's tendency to stain the UV LED quartz windows and reduce light transmission. Upon selection of a new witness dye, control tests were completed to determine the witness dye's behavior in the presence of UV light and hydrogen peroxide individually. These tests established a control baseline. A UV LED driven AOP was used to oxidize a witness dye in a flow through reactor vessel. Outflow from the reactor flowed into a spectrophotometer to measure the reduction in dye concentration.

Assumptions/Limitations

While the actions of this thesis research seek to expand the understanding of UV LED use in an AOP, the context and bounds of the research provide an important backdrop for the methods used, data collected and analyzed, and the results presented.

This study follows the work of preceding theses, and parallels complementary research avenues. The research and experiments follow work performed by five 2014 AFIT MS students sponsored by the EPA. Specifically, this research expands upon research conducted by Captain Kelsey Duckworth, USMC. Captain Duckworth's work focused on investigation of the effect UV LED drive patterns on the oxidation of a methylene blue witness dye in a flow-through reactor. Additional sponsored LED research avenues included: the design of the experimental reactor, spectrum characterization of UV LEDs, use of UV LEDs against bacterial spores, and modeling of UV LED light transmission in water.

There are several limitations of this research, which are described as follows and accompanied by assumptions used in the development of this study. Small, low-power UV LEDs were used in experiments. Due to the small number of manufacturers producing UV LEDs, the selection of UV LEDs available for use in this study was limited. The experiments of this research were conducted with small, low-power, UV LEDs under the assumption that the experimental findings will be adaptable to larger and more powerful UV LEDs as they become available. Additionally, due to the limited availability of commercially procurable UV LEDs, those used in this research were sourced from a single supplier (Sensor Electronic Technology, Inc.). Other manufacturers were contacted but were unable to provide viable UV LEDs in the timeframe required. Due to laboratory safety and waste disposal requirements, a witness dye, not toxic contaminants, was used to indicate the effects of the UV LED driven AOP. The findings of this research are limited to description of the UV LED driven AOP.

Studies on the effect of the UV LED driven AOP on chemicals with properties similar to target contaminants should be the focus of future research.

The experiments used a small flow-through reactor designed for experimentation. This reactor design does not represent a potential design for a mass decontamination system. Research findings on the performance of the UV LEDs used in this reactor will be assumed as potentially useful in reactors of different designs. Further research will be needed to determine optimal reactor design; however, such analysis is outside the scope of this study. While fluid flow dynamics and turbidity would have an effect on real-world fluid decontamination, their complexity in relation to the current stage of this research places them outside the scope of this study. This limitation means that the findings of this study will not be directly applicable to decontamination of flowing turbid waters.

Overview

This chapter described the problem this thesis investigated and outlined the background of the use of UV LEDs in an AOP for water decontamination. It denoted research and investigative questions, described the bounds and limitations of the research, and summarized the research methodology. In the remainder of this document, the literature review discusses sources relevant to the use of UV LEDs in an AOP; it also provides context and theory for the research methods. The methods chapter describes the methods of experimentation for addressing the research and investigative questions. All hypotheses, experimental procedures, data collection processes, materials, and equipment are thoroughly described in the methods chapter. Analysis, arrangement, and

presentation of the collected data are described in the results chapter. Discussion of the research findings, to include their significance and reliability are presented in the final chapter.

II. Literature Review

The purpose of this chapter is to review the relevant literature on the background of the research along with key areas relevant to the use of UV LEDs in Advanced Oxidation Processes. These vital areas include: UV light and use, UV Advanced Oxidation Processes, use of witness dyes in experimentation, LED properties and advancements, and the use of UV LEDs in AOPs.

Background

Contamination of surface waters, originating from either malicious or accidental sources could pose a threat to public safety. The United States National Security Strategy states: “there is no greater threat to the American people than weapons of mass destruction,” which includes attacks using chemical and biological weapons (The White House 2010). In early 2014, an industrial chemical tank leaked into the Elk River, upstream from a water treatment plant, which supplies drinking water to sections of the Charleston, West Virginia, metropolitan area. The spill contaminated the water supply for 300,000 residents and caused 300 to require medical treatment (Barrett 2014). In early August of 2014, 500,000 residents of Toledo, Ohio, were advised not to use tap water due to high levels of microcystin, a toxin that originates from algae and can cause diarrhea, vomiting, and even affect liver function (Fitzsimmons 2014). The threat of terrorism and instances like these have prompted the U.S. Environmental Protection Agency (EPA), National Homeland Security Research Center, Water Infrastructure Protection Division, to sponsor research on processes which may prove useful in decontamination following such an event.

UV Light and Usage

Ultra violet light resides just below visible light on the electromagnetic spectrum as shown in [Figure 1](#); due to its higher energy photons it can play a role in many chemical reactions. The UVC range of UV light includes wavelengths from 200-280 nm, which are capable of rendering microorganisms ineffective by disrupting their DNA and preventing reproduction (Crystal IS 2013). While water treatment plants have traditionally turned to chemicals such as chlorine to disinfect water, the use of UVC light presents some substantial advantages. UVC light can deactivate the chlorine resistant microorganism cryptosporidium and giardia, does not require harsh chemicals, has no known toxic by-products, and does not affect the taste or smell (Crystal IS 2013).

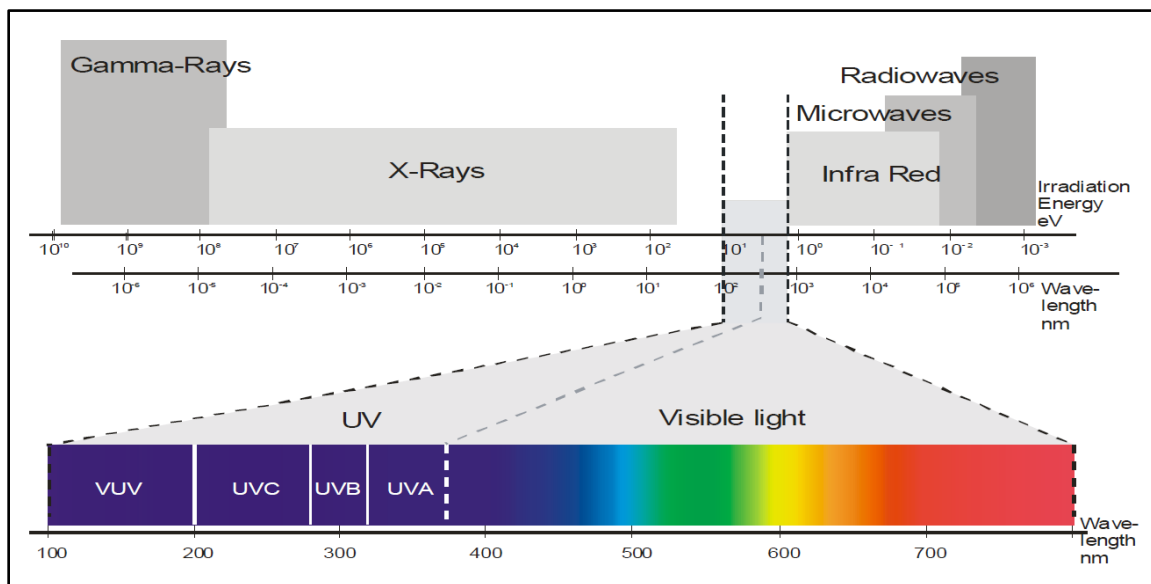
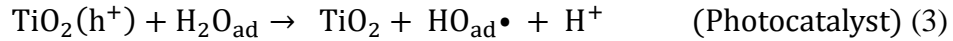
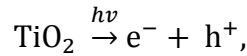
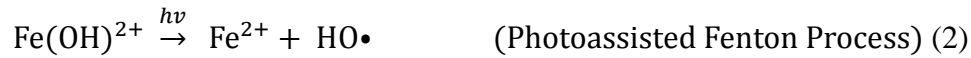
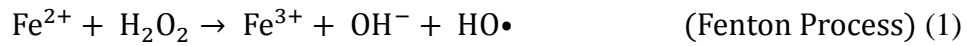


Figure 1 - Electromagnetic Spectrum (Crystal IS 2013)

Advanced Oxidation Processes (AOPs)

In addition to being useful for water disinfection, UV light can be used to drive Advanced Oxidation Processes (AOPs). AOPs are powerful chemical processes that center on the

generation and use of the highly reactive hydroxyl (HO) radical to oxidize harmful organic compounds with the aim of mineralizing the compounds into carbon dioxide, water, and inorganic material, or at least decompose them into less harmful products (Andreozzi, et al. 1999). Multiple advanced oxidation processes utilize differing reactants and catalysts to produce hydroxyl radicals; these processes are shown in equations 1-4 (Andreozzi, et al. 1999).



The process of primary interest for this research is the photolysis of H_2O_2 by UV light with a wavelength of 280nm or less. The UV/ H_2O_2 AOP is of particular interest because Autin et al. (2013) found it to be more effective than UV/ TiO_2 in terms of quantum yield and energy consumption. The UV/ H_2O_2 process has been evaluated in multiple studies; Bounty et al. (2012) conducted experiments to evaluate the effectiveness of the AOP against adenoviruses. Their study focused on the adenovirus due to its resistance to disinfection by UV alone and the multiple maladies that adenoviruses cause in humans. Their experiments showed that the UV/ H_2O_2 AOP enhanced adenovirus

inactivation by a 0.44-1.7 log magnitude, with variations depending on UV dosage and H_2O_2 concentration (Bounty, Rodriguez and Linden 2012). AOPs could also be useful in situations like the microcystin contamination of Toledo's tap water. Researchers in South Korea used AOPs, including UV/ H_2O_2 , to destroy *Escherichia coli* and degrade the endotoxin released by the destruction of the bacteria's membrane (Oh, et al. 2014). Their study sought a method to not only address the health hazard presented by the *Escherichia coli* bacteria, but also the endotoxin from the cell membrane, which is released during typical disinfection protocols that only destroy the bacteria.

These studies demonstrate the power and versatility of AOPs and their potential usefulness in the decontamination of water. AOPs work well with UVC light and can be integrated in a single water treatment system which address both the destruction of bacteria and organic compounds.

Witness Dye Use in Research/Experimentation

Using a witness dye as a surrogate for a chemical contaminant provides researchers with a method to determine the AOP reaction rate and provides more safety than working directly with a contaminant. Experimentation by Duckworth (2014) utilized methylene blue to serve as an indicator dye; during the UV/ H_2O_2 AOP, the dye decolorizes when exposed to OH radicals and serves as a reaction rate indicator. Post thesis experimentation indicated that the methylene blue dye stained the windows of the UV LEDs sufficiently to significantly decrease the flux output of the LEDs, which may have affected the reaction rate of the AOP (Duckworth, et al. In Review).

This staining and corresponding reduction in transmission precipitated a search for other suitable dyes for UV LED driven AOP experimentation. During post research discussion on the staining, the US EPA Water Infrastructure Protection Division suggested that the staining might be partially attributable to methylene blue's cationic properties causing it to affix to the anionic quartz UV LED windows (Phillips 2014). In light of this possibility, researchers at the US EPA suggested the use of Brilliant Blue FCF as an indicator dye (Phillips 2014).

Brilliant Blue FCF dye is frequently used as a colorant in the foodservice industry to give food and beverages a blue color (Gosetti, et al. 2004). The dye exhibits low toxicity, is neutral and anionic, and does not readily adsorb onto negatively charged particles. Due to low toxicity and reactivity, Brilliant Blue FCF is the most predominantly used dye to track fluid paths through soil (Flury and Wai 2003). Additionally Brilliant Blue FCF, known also as Acid Blue 9 and FD&C Blue No. 1, is used to control aquatic plants in ponds and color toilet bowl cleaners (Flury and Fluhler 1994). Experiments conducted by Handa et al.(2007) showed that OH radicals work to decompose and decolorize Brilliant Blue FCF as a witness dye.

To be useful in AOP experiments, the witness dye should not degrade readily in the presence of solely UV light. Field studies of Brilliant Blue FCF have shown it to degrade rather slowly when used in ponds as an algaecide, showing a degradation half-life up to two months (Flury and Fluhler 1994). Other studies indicate that Brilliant Blue FCF shows good light stability when used in foods and drinks (Flury and Fluhler 1994). The purported resistance to degradation of Brilliant Blue FCF by light indicates it may be a good candidate as a witness dye for the UV/H₂O₂ AOP.

LED Properties and UV Advancements

LEDs are semiconductors that emit light when different polarity carriers combine to generate a photon; the wavelength of the photon is determined by the type of carriers present (Bettles, et al. 2007). Visible light LEDs have made significant advances in the past decades. Similar to Moore's Law for microprocessors, which theorized that microprocessor performance would double each year, Roland Haitz theorized, based on the study of LED development, that visible LED luminous output would increase at a rate of 35% per year as the per lumen cost would correspondingly decrease by 20% per year (Lenk and Lenk 2011). Lenk and Lenk (2011) compared the predictive model of Haitz Law with actual improvements in LED efficacy and verified that such rapid increases are truly occurring. These increases are anticipated to continue until the efficacy of visible LEDs reaches its theoretical limit, at which time the luminous output will stabilize while the price will continue to decrease (Lenk and Lenk 2011).

Some of the advantages LEDs exhibit over other light sources include high durability, light weight, high efficiency, long life, instantaneous start-up, high energy density, and the ability to withstand multiple on-off cycles (Lenk and Lenk 2011, Bettles, et al. 2007). While visible light LEDs represent a maturing technology, UV LEDs are still in the early stages of development (Bettles, et al. 2007). Although current UV LED efficiencies are in the single digit percentage range only, researchers anticipate that advancement in UV LEDs will likely follow Haitz's Law and rapidly advance (Bettles, et al. 2007, Würtele, et al. 2011, Autin, Romelot, et al. 2013).

Mercury-based fluorescent lamps currently provide the UV light for various disinfection and decontamination processes (Würtele, et al. 2011, Bettles, et al. 2007).

Use of these lamps could result in the release of toxic mercury into the environment should a lamp break (Bettles, et al. 2007). Additionally, mercury lamps have the disadvantages of large size, limited lifespan, high power requirements, and require a warm-up period prior to use (Würtele, et al. 2011). UV LEDs have the potential to replace mercury lamps in many UV processes, as well as open the door to new applications of UV light based on their unique characteristics (Bettles, et al. 2007, Würtele, et al. 2011). Although current UV LED technology lacks the power and affordability for widespread use, assessments based on the forecasted advances in UV LED technology predict technical and economical viability near the year 2020 (Bettles, et al. 2007, Autin, Romelot, et al. 2013).

UV LEDs in AOPs

While most data on AOP experimentation are based on experiments that use mercury lamps, some more recent studies have utilized UV LEDs. Autin et al.(2013) used UV LEDs to drive UV/H₂O₂ and UV/TiO₂ AOPs to degrade methylene blue and metaldehyde in solution. Their experiments found that similar UV light exposure levels from UV LEDs and traditional mercury lamps produced similar removal levels (Autin, Romelot, et al. 2013). Their work shows that UV LEDs are capable of driving AOPs comparable to current mercury vapor lamps. However, two unique differences exist between these technologies which have the potential to alter this comparison. First, LEDs emit light in only a narrow wavelength band and can be manufactured with any of a large range of center wavelengths while traditional mercury lamps either emit light primarily at 254 nm, as is the case for low pressure mercury lamps, or over a range of

wavelengths, as is the case for high pressure mercury lamps (Würtele, et al. 2011). If it is found that particular wavelengths of light are particularly effective in AOP, or more likely disinfection; this property may provide additional benefits for UV LEDs. Secondly, LEDs can be rapidly switched on and off while mercury lamps require a significant warm-up period and are, therefore, constrained to continuous operation. If it is found that AOPs performed with pulsed illumination is more effective than continuous illumination, the instant on-off capabilities of LEDs may provide a further advantage.

Summary

Effective methods for the decontamination of waters fouled by industrial accidents, naturally occurring environmental contaminants, or terrorist acts constitute a vital capability for the protection of the American people. Advanced oxidation processes (AOPs) may provide a powerful tool for these decontamination operations when combined with the emerging technology of UV LEDs. Research on UV/H₂O₂ AOP oxidation of contaminants, and contaminant surrogates, indicates potential viability for decontamination.

III. Methodology

To address the primary research question, multiple experiments were conducted. The first experiment collected observations on the effect of methylene blue staining of the quartz LED windows on light output. Additional preparatory experiments established controls for dye staining of UV LEDs, UV effects on the witness dye, and H₂O₂ effects on the witness dye. The core experiments evaluated the effect of differing UV LED duty cycles on hydroxyl radical production by measuring the change in concentration of a witness dye over time. These experiments mimicked the experiments completed by Duckworth (2014) with methylene blue but employ a different witness dye and focused on different duty cycles. This chapter describes the theory behind the experiments and data collection methods. It also describes the materials and equipment utilized during the experiments; finally it explains the experimental setup and the procedural steps used to conduct the research.

Theory

This research continues work examining the role of the duty cycle of UV LEDs in the production of hydroxyl radical in the UV/ H₂O₂ advanced oxidation process using a witness dye as a surrogate for a hazardous chemical contaminant. Previous research produced staining of the UV LED windows used in the methylene blue experiments. This staining was attributed to ionic attraction of the cationic methylene blue to the anionic quartz windows on the LEDs. As a result, the sponsor requested the selection of a different dye, which is believed not to exhibit this same ionic attraction and therefore would be less likely to exhibit significant staining (Phillips 2014). Research indicated

that Brilliant Blue FCF would decompose and decolorize in the presence of hydroxyl radicals and may be less likely to adsorb onto the quartz lens of the UV LEDs (Handa, Minamitani and Higashiyama 2007, Flury and Fluhler 1994).

Materials and Equipment

The process of cleaning the methylene blue stained UV LEDs for measurement utilized Kimtech Kimwipes[®] (Kimberly-Clark, Dallas, TX) soaked with a 30% solution of methanol. The experimental solution consisted of hydrogen peroxide (30% in water from Fisher Scientific, Pittsburgh, PA), Fluka analytical standard powder form Brilliant Blue FCF (Erioglaucine disodium salt) (purity 96.5% (HPLC) from Sigma-Aldrich, St. Louis, MO), and reverse osmosis purified deionized water.

A Labsphere[®] integrating sphere (Labsphere[®] North Sutton, NH) calibrated with a D2 Deuterium lamp (S/N 667329) measured luminous flux and optical power of the UV LEDs. Illumia[®] Pro software analyzed the data output from the integrating sphere and provided total power and peak wavelength data on the light source being evaluated.

The advanced oxidation process duty cycle experimentation utilized a flow-through reactor constructed of a three-inch long, three-inch diameter tube of electro polished 316 stainless steel with one-inch diameter inflow and outflow tubes and flat endplates with a total volume of 350 ml (Spencer 2014). One of the reactor endplates held seven 245 nm UV LEDs from Sensor Electronic Technology, Incorporated, Columbia, SC. The reactor configuration is shown in [Figure 2](#).

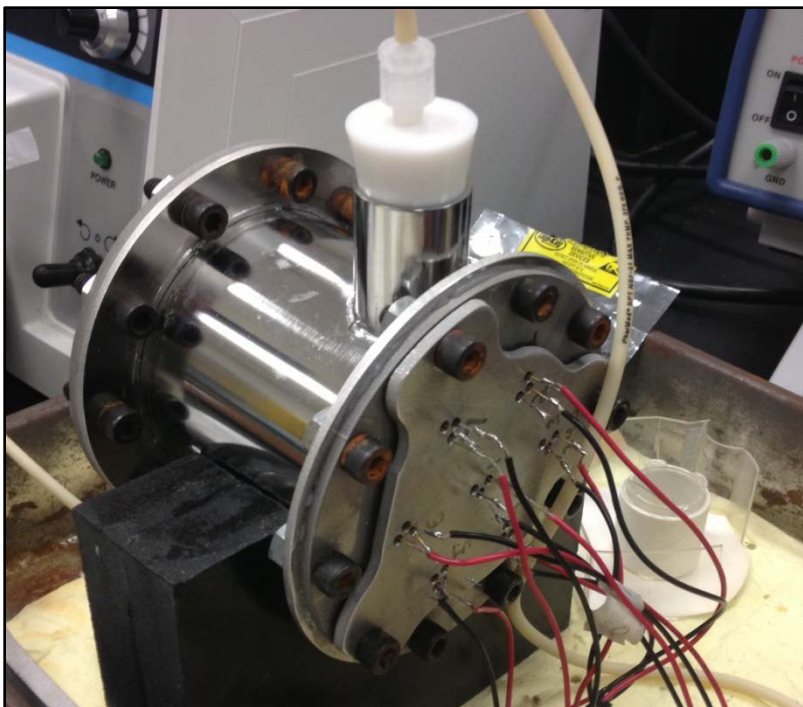


Figure 2 - Flow-through Reactor with UV LEDs

A control signal for the reactor's LEDs originated from Data Acquisition System Laboratory (DASYLab, version 12, Stamford, CT) software installed on a laptop computer. The program controlled the input of the varied duty cycles used in the experiments; it was connected through a driver box (Measurement Computing device: USB-2408-2AO, Norton, MA) that controlled a driver board which delivered power to the reactor's LEDs. This driver board, developed and constructed by Duckworth (2014) and Spencer (2014), utilized LUXdrive DynaOhm (4006-020 1338, Randolph, VT) resistors to maintain a current of 20mA to each LED (K. L. Duckworth 2014). An oscilloscope (OWON PDS5022T, Zhangzhou, China) was used to verify that the voltage and current to the UV LEDs from the driver board corresponded to the desired duty cycle for each experiment.

A MasterFlex Console Drive (model number 77521-50, Gelsenkirchen, Germany) propelled the flow of the experimental solution at a rate of 0.7 or 1.4 milliliters per minute through PharMed[®] BPT tubing (inner diameter of 0.8 millimeters, Valley Forge, PA) (K. L. Duckworth 2014). The solution flowed from the new material flask, through the console drive, and into the reactor where it directly contacted the quartz lenses of the UV LEDs and reacted with the UV light. The solution flowed into the bottom of the reactor and out through the top (reactor oriented with endplates perpendicular to the ground). Upon exiting the reactor, the solution flowed through an Agilent Technologies Cary 60 UV-Vis Spectrophotometer (Santa Clara, CA) which measured the absorption of the 630nm wavelength light, the absorbent peak for Brilliant Blue FCF dye, every five minutes (Handa, Minamitani and Higashiyama 2007, K. L. Duckworth 2014). [Figure 3](#) provides a visual representation of the flow of electrical signals to the UV LEDs and the flow of the experimental solution through the experimental apparatus.

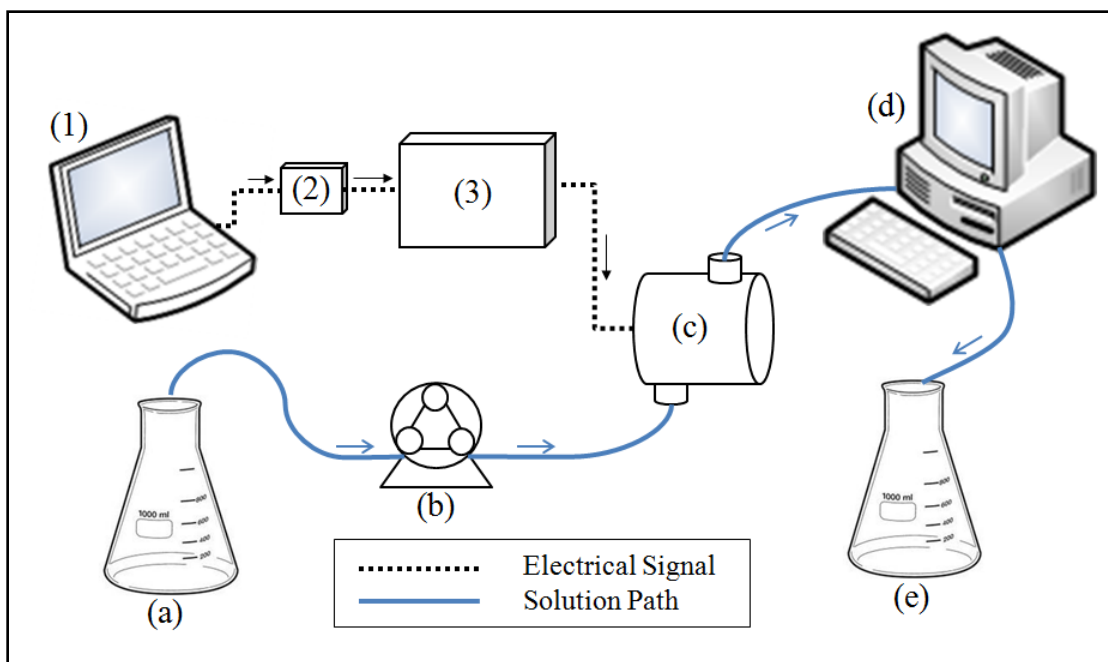


Figure 3 - Advanced Oxidation Process Experimental Setup. Electrical signal to the reactor UV LEDs follows the numbered sequence originating from a laptop (1) running DASYLab software, which sends the signal to the driver box (2) that pushes the duty cycle signal to the driver board, which provides the proper signal to all seven UV LEDs in the reactor vessel (c). The reactor is fed with the experimental solution of 5-millimolar (mM) hydrogen peroxide and 0.01-millimolar (mM) Brilliant Blue FCF originating at the feed vessel (a). A peristaltic pump (b) propels the solution through the UV LED reactor (c) at flow rates of 0.7 ml/min and 1.4 ml/min. The solution flows from the reactor through the UV-Vis Spectrophotometer (d), which measures its absorbance of 630nm light, and into the waste collection vessel (e)

The solution of reactants for all UV/ H₂O₂ advanced oxidation process duty cycle experiments consisted of 5-millimolar (mM) hydrogen peroxide and 0.01-millimolar (mM) Brilliant Blue FCF. To mix one liter of the experimental solution, 5 ml of a 2-millimolar (mM) stock solution of Brilliant Blue FCF and deionized water were combined with 0.5669 grams of hydrogen peroxide (30% in water from Fisher Scientific, Pittsburgh, PA), and diluted with reverse osmosis deionized water until the volume of the solution reached one liter. The 2-millimolar (mM) stock solution of Brilliant Blue FCF and deionized water was comprised of 0.1643 grams of Fluka analytical standard powder

form Brilliant Blue FCF (Erioglaucine disodium salt) (purity 96.5% (HPLC) from Sigma-Aldrich, St. Louis, MO) combined with 50 ml of deionized water in a 100 ml volumetric flask. The flask was then closed with a stopper, sealed with paraffin tape, and placed in a wrist shaker for 2 hours. After the initial mixing, deionized water was added to the solution until the total solution volume equaled 100 ml to reach the 2-millimolar (mM) stock solution concentration; the flask was then reclosed, resealed and returned to the wrist shaker for an additional 30 minutes of mixing.

Calibration of the Agilent Technologies Cary 60 UV-Vis Spectrophotometer (Santa Clara, CA) to the concentration levels of Brilliant Blue FCF dye in the experimental solutions utilized a five-point calibration curve to correlate light absorbance values of the solution with concentration levels of the witness dye. The five points of the calibration curve consisted of 0.0100-millimolar (mM), 0.0075-millimolar (mM), 0.0050-millimolar (mM), 0.0025-millimolar (mM), and 0.0000-millimolar (mM) levels of Brilliant Blue FCF dye. These concentration levels correspond to the 100%, 75%, 50%, 25%, and 0% levels of the original dye concentration in the experimental solution. Calibration samples were prepared by filling cuvettes with the experimental solution (full, $\frac{3}{4}$ full, $\frac{1}{2}$ full, $\frac{1}{4}$ full and none) and filling the rest of the cuvette with reverse osmosis purified deionized water, which yielded the calibration concentrations. Each of the cuvettes was then placed in the Spectrophotometer to acquire the light absorbance values for the respective concentrations of witness dye in the solution.

Determining the Effect of Methylene Blue Adsorption on Power Output

To collect data on how methylene blue staining affected LED output, the UV LEDs from the previous experiments were disconnected from the electrical connections to the driver board and extracted from the reactor vessel. The stained LEDs were then placed in the Labsphere[®] integrating sphere where the LED center wavelength (nm), selected power (230 nm - 265 nm) (W), and total power (W) as shown by the Illumia[®] Pro software were recorded. The stained LED was then wiped with a methanol soaked Kimwipe[®] until the quartz LED lens showed no blue tint as observed by the naked eye (approximately 60 seconds of wiping). The cleaned LED was then placed back in the Labsphere[®] integrating sphere, where the LED center wavelength (nm), selected power (230 nm - 265 nm) (W), and total power (W) as shown by the Illumia[®] Pro software were recorded once again. This procedure was executed individually for each of the seven LEDs extracted from the reactor to prevent interchanging the non-serialized UV LEDs and to ensure the tinted and cleaned measurements were of the same LED.

UV LED Quartz Lens Adsorption Experiment

While Brilliant Blue FCF is an anionic substance, and studies indicated that it does not readily adsorb onto negatively charged surfaces, experiments were performed to characterize any tinting that may take place due to the dye. Because staining of the LED windows by methylene blue may have affected the results of the experiments performed by Duckworth (2014), these experiments started by testing the adsorption of Brilliant Blue FCF on to the quartz lens of the UV LEDs. The experiment measured the output of nine UV LEDs before they were placed in a 0.01-millimolar (mM) solution of Brilliant

Blue FCF and then removed three at a time from the dye solution at intervals of 12, 24, and 48 hours. Each of the LEDs was placed in the Labsphere[®] integrating sphere, and the LED center wavelength (nm), selected power (230 nm - 265 nm) (W), and total power (W) as shown by the Illumia[®] Pro software were recorded. The quartz lens of the LED was then wiped with a methanol soaked Kimwipe[®] until clean. The clean LED was then returned to the Labsphere[®] integrating sphere and the LED center wavelength (nm), selected power (230 nm - 265 nm) (W), and total power (W) as determined by the Illumia[®] Pro software were once again recorded. This procedure was repeated with all three sets of three UV LEDs. The solution consisted of a 0.01-millimolar (mM) solution of Brilliant Blue FCF comprised of 5 ml of a 2-millimolar (mM) stock solution of Brilliant Blue FCF and 995 ml of deionized water.

In addition to testing the adsorption of Brilliant Blue FCF onto the quartz UV LED lenses, this experiment was also conducted with Methylene Blue as a comparison. The comparison experiment measured the output of nine UV LEDs placed in a 0.01-millimolar (mM) solution Methylene Blue, which were removed three at a time from the dye solution at intervals of 12, 24, and 48 hours. Output testing was performed on each UV LED as described previously. The 0.01-millimolar (mM) solution of Methylene Blue consisted of 0.00379 grams of Methylene Blue powder (Fischer Scientific Biological Stain) combined with deionized water until the volume of solution reached one liter.

UV Brilliant Blue FCF Control Experiment

While studies have indicated that Brilliant Blue FCF has good light stability (Flury and Fluhler 1994), this research included control experiments to evaluate whether the UV

light from the UV LEDs exerted any degradation on the witness dye. The UV control experiment used a 0.01-millimolar (mM) solution of Brilliant Blue FCF comprised of 5 ml of a 2-millimolar (mM) stock solution of Brilliant Blue FCF and 995 ml of deionized water. This solution passed through the advanced oxidation process experimental setup, as shown in [Figure 3](#), with the UV LEDs running at a 100 percent duty cycle (constant on). The spectrophotometer measured and recorded the light absorption of the solution at five-minute intervals for 300 minutes to determine if UV light alone exerted any decolorizing effect on the dye.

H₂O₂ Brilliant Blue FCF Control Experiment

To control for any decolorizing effect that hydrogen peroxide may exert on Brilliant Blue FCF in the experimental set-up, an experiment where the dye solution interacted with H₂O₂ in the absence of UV light (0% duty cycle) was performed. The experimental solution of 5-millimolar (mM) hydrogen peroxide and 0.01-millimolar (mM) Brilliant Blue FCF flowed through the experimental set-up, as shown in [Figure 3](#), with the UV LEDs deactivated. The spectrophotometer measured and recorded the light absorption of the solution at five-minute intervals for 300 minutes to determine if H₂O₂ alone exerted any decolorizing effect on the dye.

Duty Cycle Experiments

The primary experiments of this research involved testing the effect of the duty cycle of UV LEDs on the UV/ H₂O₂ advanced oxidation process as shown through the decolorization of the Brilliant Blue FCF witness dye. The experimental solution of 5-millimolar (mM) hydrogen peroxide and 0.01-millimolar (mM) Brilliant Blue FCF

flowed through the experimental set-up as shown in [Figure 3](#) with the UV LEDs running at varied duty cycles. Duty cycle testing utilized a frequency of 9.09 hertz as used by Duckworth(2014). The experiments utilized five different duty cycle patterns: a 5 percent duty cycle (5.5 milliseconds (ms) on, 104.5 ms off), a 10 percent duty cycle (11 milliseconds (ms) on, 99 ms off), a 20 percent duty cycle (22 ms on, 88 ms off), a 30 percent duty cycle (33 ms on, 77 ms off), and a 100 percent duty cycle (constant on).

[Figure 4](#) displays a graphical representation of these drive patterns.

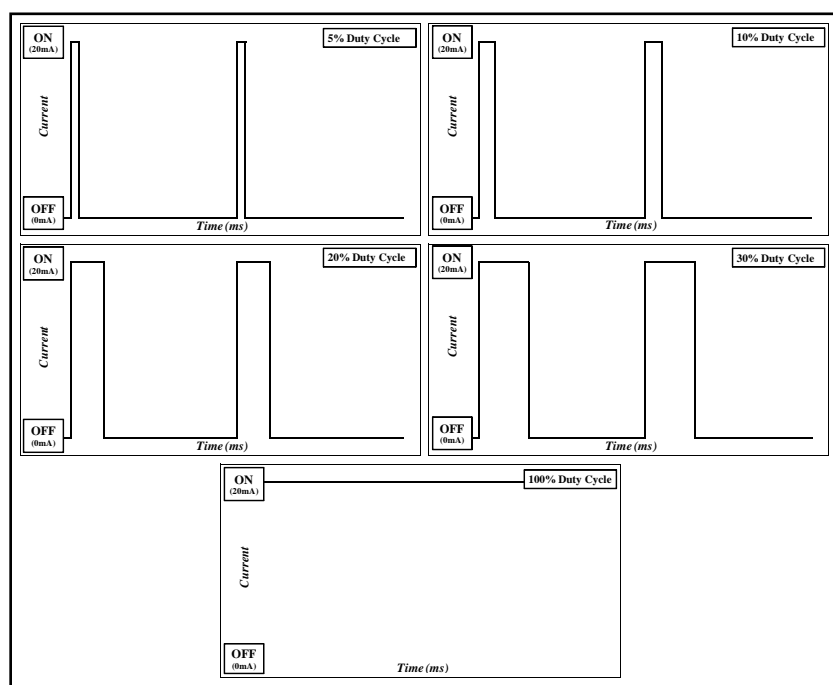


Figure 4 - UV LED Experimental Duty Cycle Drive Patterns

The spectrophotometer measured and recorded the light absorption of the solution to determine the concentration of the dye in the solution at five-minute intervals during a 300 minute interval, which was selected to be long enough to permit the concentration levels to stabilize. The decolorizing oxidation reaction was then modeled using the mass

balance equation for a complete mix reactor shown in Equation 5 (Duckworth, et al. In Review).

$$\frac{C}{C_0} = \frac{\tau k_s e^{-\left(t(k_s + \frac{1}{\tau})\right)} + 1}{\tau k_s + 1} \quad (5)$$

Where C_0 represents the original concentration of dye in the solution at the start of the experiment; C represents the dye concentration at time, t , after the experiment start; τ represents the residence time of the solution in the reactor and was calculated using Equation 6, where V represents the volume of the reactor and Q equals the flow rate of the solution (shown calculated for the two experimental flow rates of 1.4 ml/min and 0.7 ml/min respectively).

$$\tau = \frac{V}{Q} = \frac{350 \text{ ml}}{0.7 \text{ ml/min}} = 500 \text{ min} \quad \frac{350 \text{ ml}}{1.4 \text{ ml/min}} = 250 \text{ min} \quad (6)$$

Comparison of the hydroxyl generation of the varying duty cycles of UV LEDs used the computed rate constant (k_s) value of the best fit model based on Equation 5. Evaluation of hydroxyl radical production in relation to duty cycle/energy input used an adjusted rate constant ($k_{s \text{ adj}}$) where the rate constant was normalized by dividing it by the UV LED duty cycle as shown in Equation 7.

$$k_{s \text{ adj}} = \frac{k_s}{dc} \quad (7)$$

This adjustment normalized the rate constant by the duty cycle, which was proportional to the integrated current. Assuming that the integrated current is then proportional to the

quantum flux of the LEDs as observed by Bates(2014), this normalization adjusts the rate constant to normalize the conditions according to equivalent quantum efficiency of the LED output.

Summary

Research on the use of UV LEDs in Advanced Oxidation Process consisted of multiple experiments. The initial experiments collected observations on the effect of methylene blue staining of the quartz LED windows on light output and compared the adsorption of Brilliant Blue FCF to methylene blue with adsorption tests of the UV LED quartz lenses. The control experiments measured the effect of UV and H_2O_2 on the Brilliant Blue FCF witness dye independently. The primary research experiments evaluated the effect of differing UV LED duty cycles on hydroxyl radical production by measuring the change in concentration of a witness dye over time.

IV. Analysis and Results

Data generated through measurements and experimentation contributed to answering the investigative questions and the overall research question. Measurements showed substantial adsorption of methylene blue onto the quartz lenses of the UV LEDs after the completion of previous AOP experiments (K. L. Duckworth 2014).

Comparative immersion testing of unpowered UV LEDs in methylene blue and Brilliant Blue FCF showed that the dye type was a significant factor in the reduction of light transmitted through the lens of the UV LED. Control tests to determine the effect of both UV light and H_2O_2 on the witness dye Brilliant Blue FCF found it to be stable in the presence of each independently. Analysis of the AOP reaction rates, specifically the adjusted degradation rate constant ($k_{s \text{ adj}}$), indicated a significant difference attributable to duty cycle. Results supporting each of these statements are provided within this chapter.

Effect of Methylene Blue Adsorption on Power Output

The seven UV LEDs extracted from the reactor used in completion of the previous AOP experiment employing methylene blue as a witness dye showed substantial adsorption on the quartz lens as evidenced by the blue hue left on the methanol soaked Kimwipe[®] and measurements from the Labsphere[®] integrating sphere. Total power output of the UV LEDs prior to cleaning ranged from 0.2092 milliwatts (mW) to 0.3814 mW with a mean pre-cleaning output of 0.3214 mW. Following cleaning with methanol, these outputs increased by 0.1857 to 0.2181 mW, for a post cleaning output range of 0.4273 to 0.5737 mW, with a mean output of 0.5066 mW. Selected power (230-265nm) outputs prior to cleaning ranged from 0.2083 mW to 0.2713 mW, with a mean of 0.2421

mW. Following cleaning, these outputs increased by 0.1375 mW to 0.1813 mW, for a post cleaning output of 0.3838 mW to 0.4526 mW, with a mean selected power output of 0.4079 mW.

Percentage reductions in power output were calculated by taking the difference between the outputs of the pre-cleaning LED and post-cleaning LED and dividing it by the post-cleaning LED output. The reductions in total power ranged from 30.8% to 51.0%, with a mean output reduction of 37.0%. Adsorption of methylene blue onto the quartz LED lenses reduced selected power output (230-265nm) 34.2% to 46.1%, with a mean reduction of 40.7%. ~~Figure 5~~ shows a comparison of the percentage reductions in output observed due to methylene blue adsorption onto the quartz lenses of the individual LEDs.

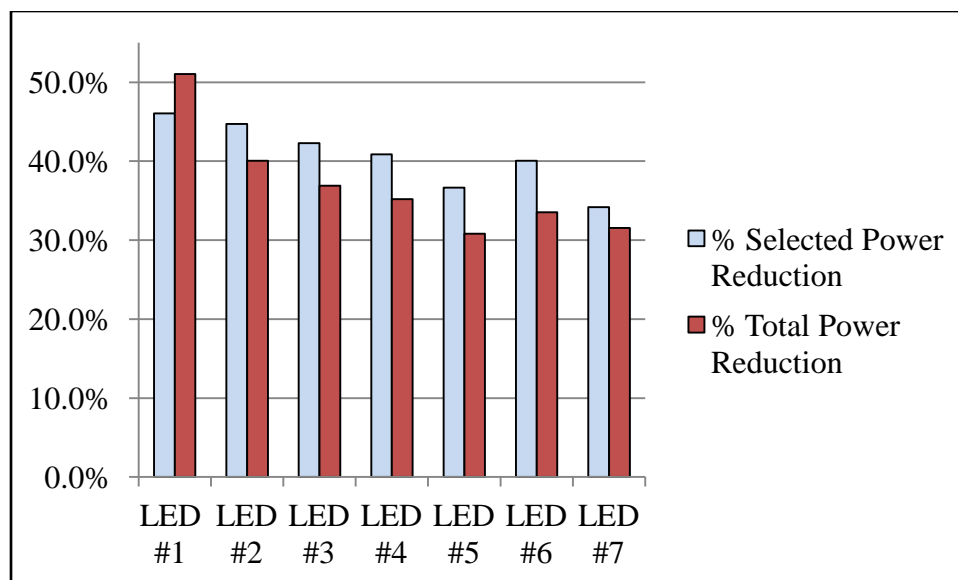


Figure 5 - Percent reduction of light output by methylene blue adsorption on post experimentation reactor UV LEDs

The nine UV LEDs used for dye adsorption testing showed much less adsorption than the UV LEDs extracted from the reactor used in previous methylene blue experimentation. The pre-cleaning total power outputs of the nine UV LEDs submerged in a 0.01 mM solution of Brilliant Blue FCF ranged from 0.4296 mW to 0.7780 mW, with a mean of 0.6745 mW. Following cleaning, these outputs increased to a range of 0.4423 mW to 0.7822 mW, with a post-cleaning mean of 0.6803 mW. Selected power (230-265nm) outputs prior to cleaning ranged from 0.4084 mW to 0.5217 mW, with a mean of 0.4465 mW. These values increased to a post-cleaning output of 0.4180 mW to 0.5223 mW, with a mean post cleaning selected power output of 0.4516 mW. Percentage reductions in power output were calculated by taking the difference between the outputs of the pre-cleaning LED and post-cleaning LED and dividing it by the post-cleaning LED output. The reductions in total power ranged from 0.2 % to 2.9%, with a mean output reduction of 1.0%. Brilliant Blue FCF adsorption reduced selected (230-265nm) power

out from 0.1% to 2.7%, with a mean output reduction of 1.2%. The reduction

percentages for adsorption due to Brilliant Blue FCF are shown in [Figure 6](#).

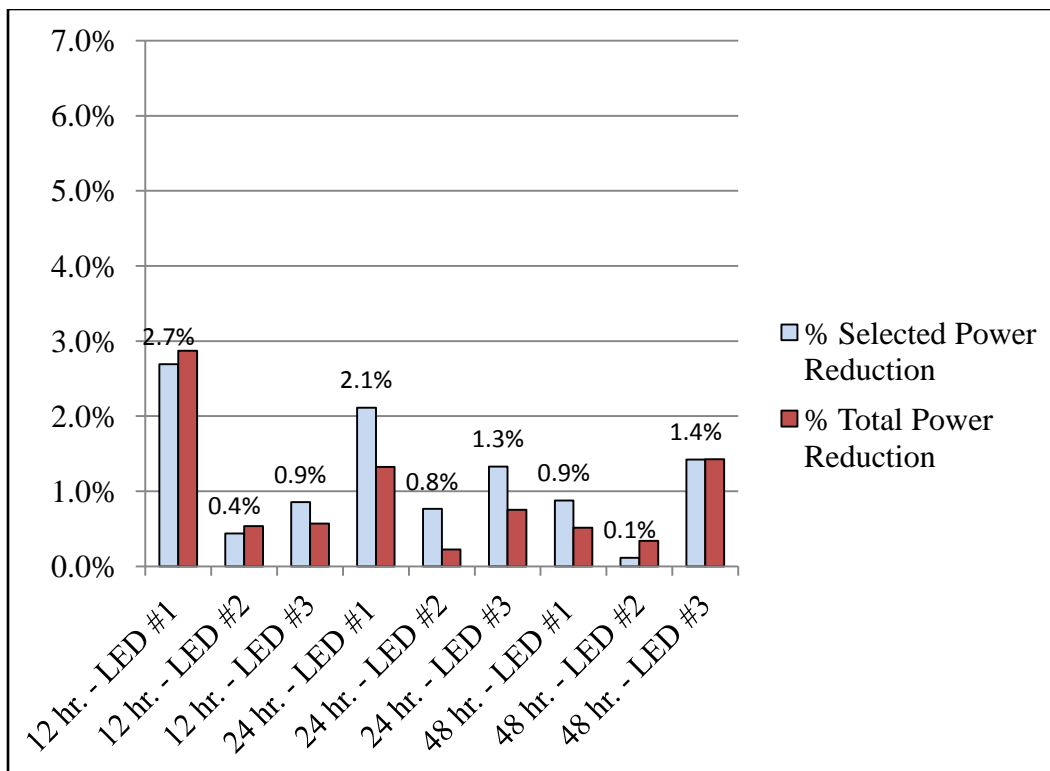


Figure 6 - Percent reduction of light output by Brilliant Blue FCF at 12, 24, and 48-hours

Adsorption testing of UV LEDs in methylene blue yielded moderately higher output reductions, although not as substantial as observed for the UV LEDs extracted from the methylene blue reactor. The pre-cleaning total power output of the nine UV LEDs placed in a 0.01-millimolar (mM) solution of Methylene Blue ranged from 0.3412 mW to 0.4441 mW, with a mean of 0.3853 mW. These values increased to a post-cleaning total power output of 0.3592 mW to 0.4756 mW with a mean of 0.3982 mW. Selected power (230-265nm) outputs prior to cleaning the methylene blue tinted UV LEDs ranged from 0.3198 mW to 0.4174 mW, with a mean of 0.3619 mW. These values

increased to a post-cleaning output of 0.3359 mW to 0.4466 mW, with a mean post cleaning selected power output of 0.3735 mW. Percent reductions in power output were calculated by dividing the difference between the outputs of the pre-cleaning LED and post-cleaning LED by the post-cleaning LED output. The reductions in total power ranged from -0.6 % to 6.6%, with a mean output reduction of 3.2%. Methylene blue adsorption reduced selected (230-265nm) power from -0.5 % to 6.5%, with a mean output reduction of 3.1%.

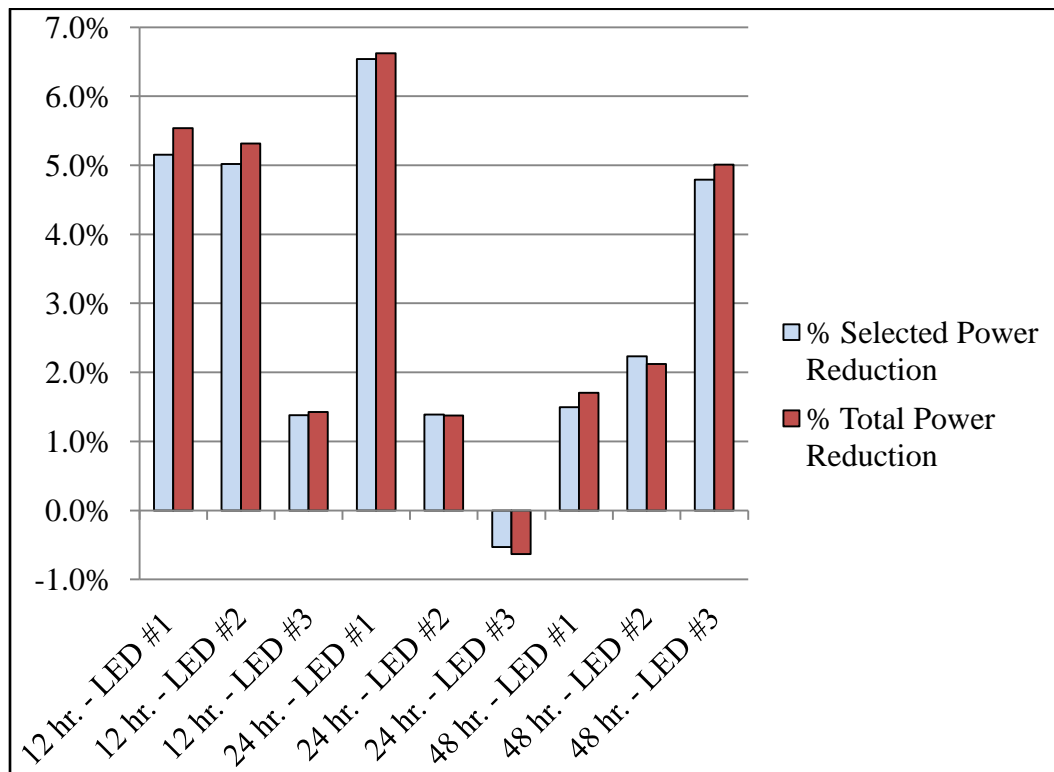


Figure 7 - Percent reduction of light output by methylene blue at 12, 24, and 48-hours

To determine whether the type of dye or the 12, 24, or 48-hour timeframes exerted a significant effect on the adsorption of the dye onto the quartz lens, a two-way analysis of variance (ANOVA) was conducted using JMP[®] analytical software. For the

two-way ANOVA, the type of dye and the timeframe served as the factors and the percent reduction in transmission served as the dependent variable. The two-way ANOVA for total power reduction found the effect of dye type was significant at $\alpha = 0.05$ (p-value = 0.0403). The two way ANOVA for select power reduction yielded significance for the dye type at $\alpha = 0.10$ (p-value = 0.0664). Neither the dye submersion timeframe nor the interaction between dye type and timeframe showed any significance in relation to the light output reduction.

To evaluate the possible effect of Brilliant Blue FCF adsorbing onto the quartz lenses of the UV LEDs during the course of the duty cycle experiments, a linear regression analysis was constructed. The linear regression evaluations compared the adjusted rate constants ($k_{s\text{ adj}}$) of the AOP reactions against both the cumulative on-time for the reactor UV LEDs and the cumulative dye immersion time for the LEDs at the beginning of the respective experimental conditions. These data are plotted in Figure 8 and Figure 9, respectively. The resulting linear regression trend lines in both comparisons show a very small negative slope, indicating only a very small negative effect of the time in the reactor on the UV LED output as indicated by the adjusted rate constant ($k_{s\text{ adj}}$). In comparison with the regression line slopes observed during preceding methylene blue experimentation, the values for Brilliant Blue FCF are substantially less. The difference in regression line slopes range from nearly two to three times less than the adsorptive experimental condition of methylene blue obtained by Duckworth et al. (In Review).

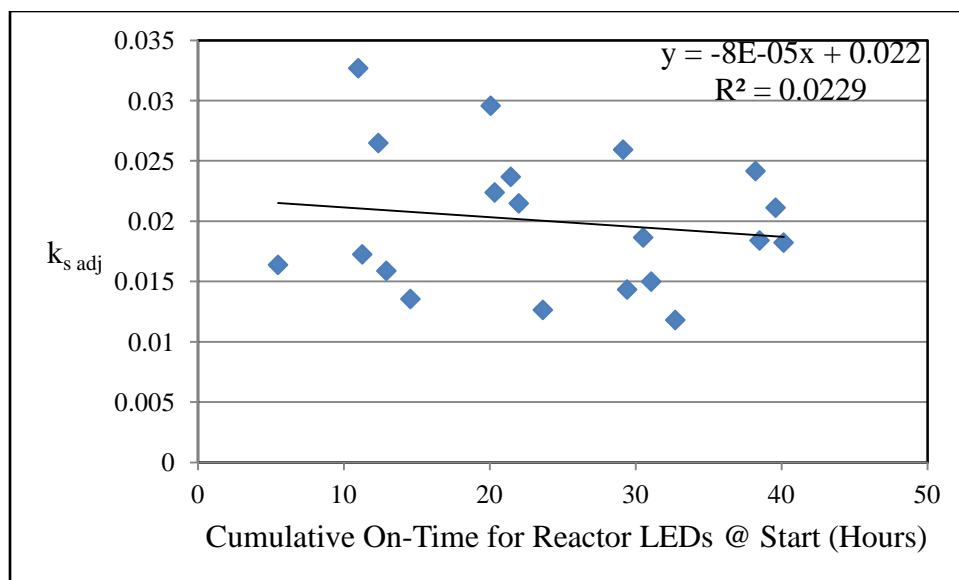


Figure 8 - Adjusted rate constant ($k_{s \text{ adj}}$) vs. cumulative on-time of reactor UV LEDs

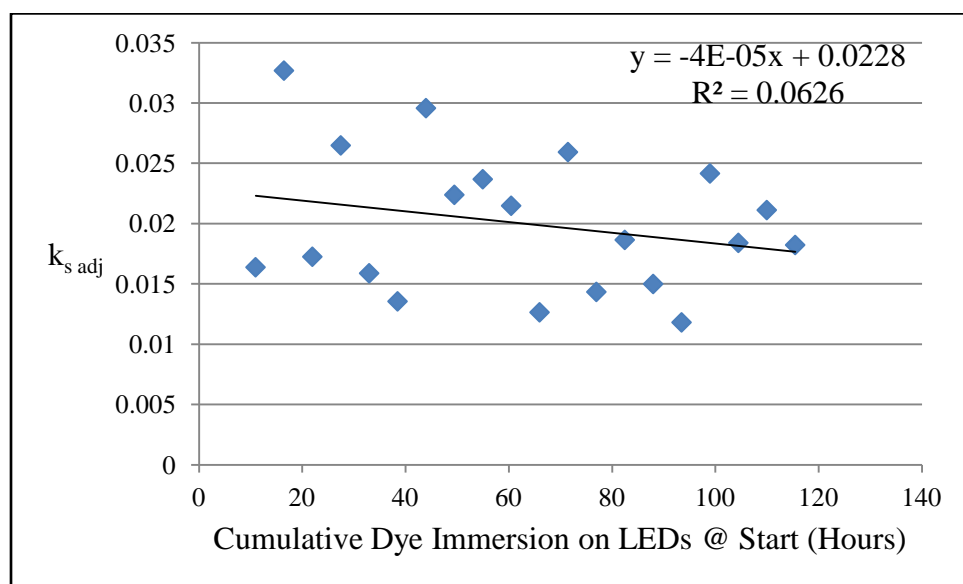


Figure 9 - Adjusted rate constant ($k_{s \text{ adj}}$) vs. cumulative immersion time of reactor UV LEDs

UV Brilliant Blue FCF Control Experiment

The control experiment to examine the possible effect of ultraviolet light on the Brilliant Blue FCF witness dye showed no degradation. As shown in [Figure 10](#), ~~Figure 10~~,

the UV light did not reduce the concentration of the Brilliant Blue FCF dye, with the data yielding an extremely small negative rate constant. These data support the assumption that the Brilliant Blue FCF dye does not become decolorized in the presence of UV light, thereby supporting its use as a witness dye for determining AOP reaction rates.

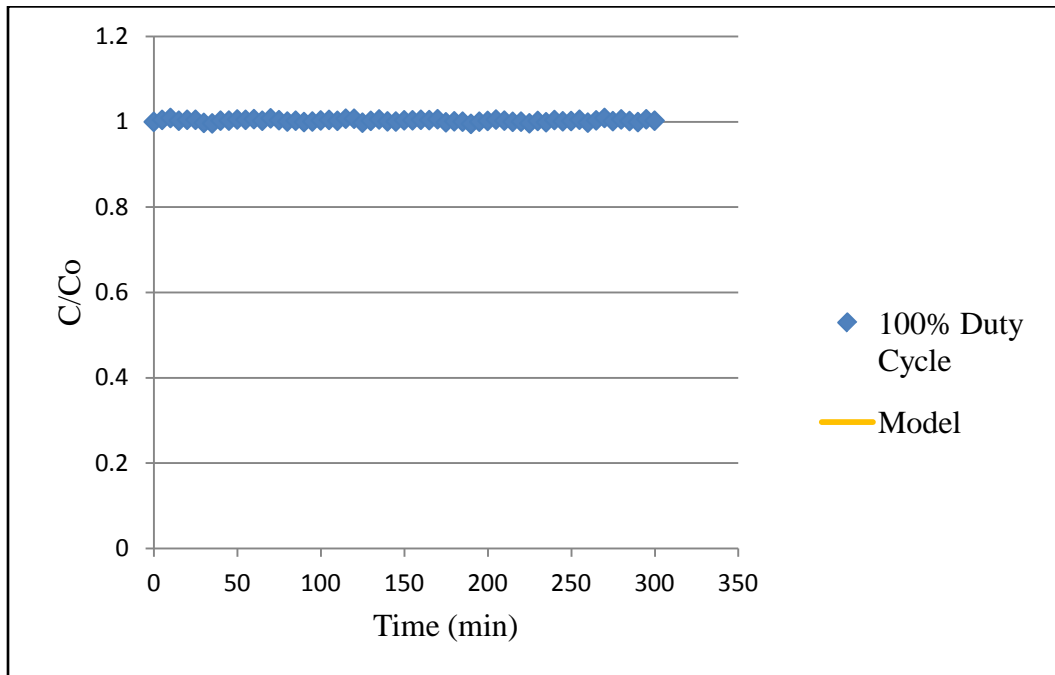


Figure 10 - UV Brilliant Blue FCF Control Experiment Results at 100% Duty Cycle

H₂O₂ Brilliant Blue FCF Control Experiment

The control experiment to examine the effect of hydrogen peroxide on the Brilliant Blue FCF witness dye also showed the dye to be stable. The results of the H₂O₂ Brilliant Blue FCF control experiment, shown in [Figure 11](#), yielded a less than one-half of one percent decrease in dye concentration. This very small reduction in concentration resulted in a rate constant of 4E-5 (min⁻¹), thus supporting the assumption that Brilliant Blue FCF and H₂O₂ do not react readily with each other in the absence of ultra violet light.

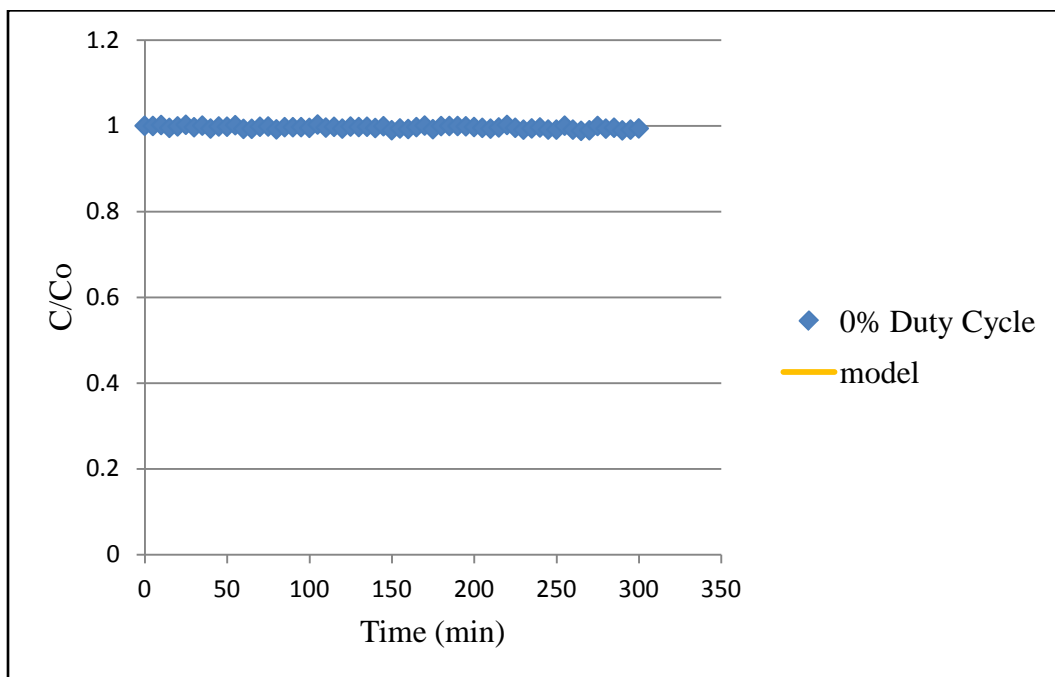


Figure 11 - H₂O₂ Brilliant Blue FCF Control Experiment Results at 0% Duty Cycle

Duty Cycle Experiments

The primary experiments to examine the effect of differing duty cycle consisted of 20 experimental conditions, two for each respective duty cycle (5%, 10%, 20%, 30%

and 100%) at each flow rate (0.7 ml/min and 1.4 ml/min). Each experiment followed the experimental procedures outlined in Appendix A for set-up and data collection. Each experiment used a five-point calibration curve, as shown in [Figure 12](#), to translate the spectrum data collected by the Agilent Technologies Cary 60 UV-Vis Spectrophotometer from light absorption values at the dye wavelength of 630 nm into concentration data using the regression line generated using Microsoft® Excel™ 2007. A new calibration curve was derived for each of the 20 experimental conditions and the two control experiments to account for any possible variance in experimental solution composition or the UV-Vis Spectrophotometer.

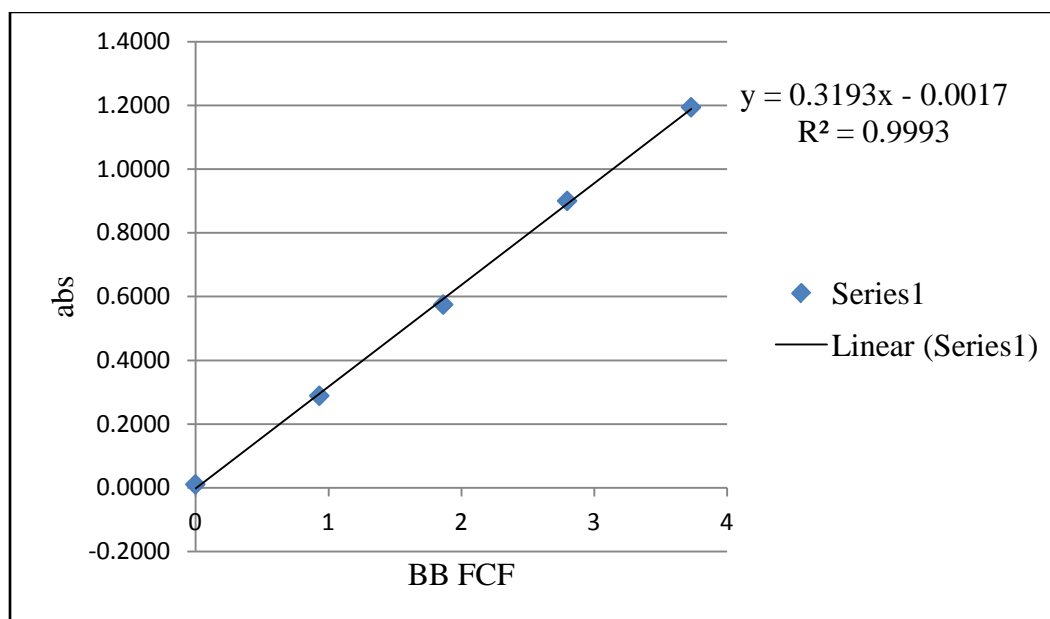


Figure 12 – Example five point calibration curve (10% duty cycle at 1.4ml/min flow rate shown)

Following concentration data collection for each duty cycle and flow rate, a linear model was fit to these data using the Microsoft® Excel™ 2007 solver function set to

minimize the sum of squares difference between the linear model line on Equation 5 and the data collected by adjusting the AOP reaction rate constant (k_s). The generated AOP reaction rate constant provides the basis for comparison of the various duty cycle and flow rate parameters. [Figure 13](#) shows an example plot of data and model line for one of the 20 experimental conditions performed.

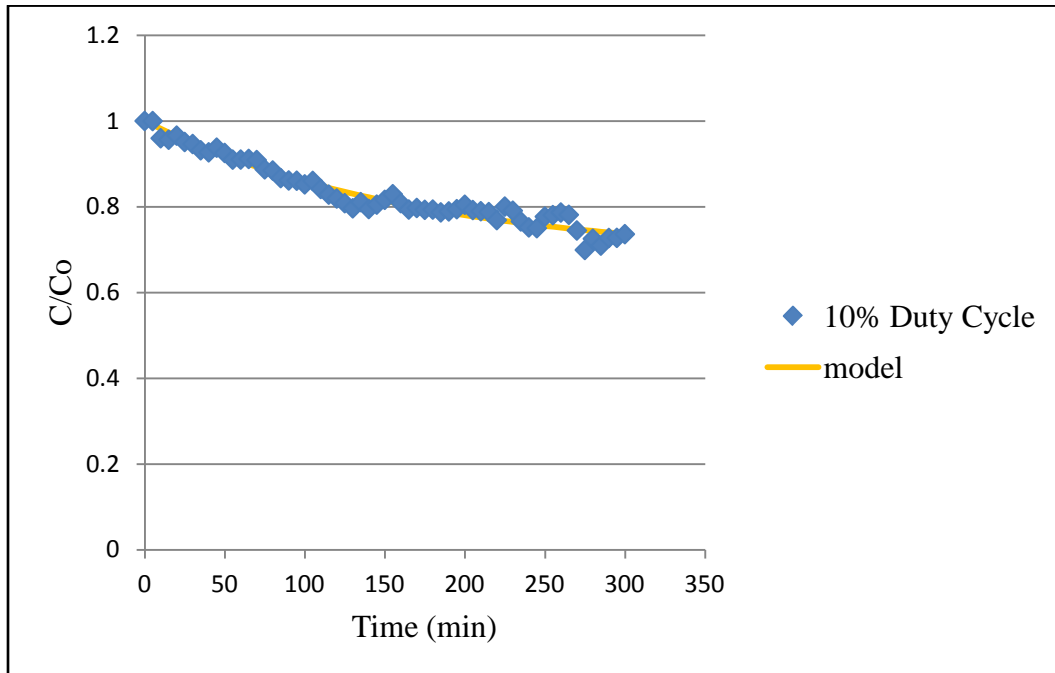


Figure 13 – Example of plotted concentration data and model curve (10% duty cycle at 1.4ml/min flow rate shown)

The majority of the data collected during the duty cycle experiments displayed good consistency. This resulted in a mean R^2 for all 20 models of 0.8445. The data from some experiments, however, showed more noise. In particular, three experimental conditions (5%, 20%, and 30%) during the first cycle of 1.4 ml/min flow rate experiments showed noise or anomalies resulting in R^2 values of 0.2773, 0.5869, and 0.5227, respectively. Excluding these data points moves the R^2 value of the all remaining

experiments to over 0.9. While the source of noise could not be ascertained, the 1.4ml/min flow rates displayed more noise than the 0.7 ml/min rates with a mean R^2 value of 0.7329 for the 1.4 ml/min versus a mean R^2 value of 0.9561 for the 0.7 ml/min flow rate. Even excluding the noisiest three values listed, the mean R^2 value is 0.8489 for the 1.4 ml/min conditions versus a mean R^2 value of 0.9561 for the 0.7 ml/min flow rate conditions. Based on the flow rate differences, the noise may stem from turbulent mixing within the reactor.

All duty cycles tested degraded the Brilliant Blue FCF dye as shown in Figure 14, with the higher duty cycles producing higher rate constants. The mean degradation rate constant (k_s) for the 100% duty cycle (continuously on) was $0.0136 \text{ minute}^{-1}$, for the 30% duty cycle the mean degradation rate constant (k_s) was $0.0053 \text{ minute}^{-1}$, for the 20% duty cycle the mean degradation rate constant (k_s) was $0.0036 \text{ minute}^{-1}$, for the 10% duty cycle the mean degradation rate constant (k_s) was $0.0022 \text{ minute}^{-1}$, and for the 5% duty cycle the mean degradation rate constant (k_s) was $0.0014 \text{ minute}^{-1}$. A two-way analysis of variance (ANOVA) was performed using JMP[®] 11 analytical software to evaluate the effects the factors of duty cycle and flow rate exerted on the degradation rate constant (k_s). The two-way ANOVA found duty cycle to be significant at $\alpha=0.05$, while flow rate and the interaction between flow rate and duty cycle were not significant. These results confirm that the difference seen in duty cycles are significant and not an artifact of statistical error or noise within the data.

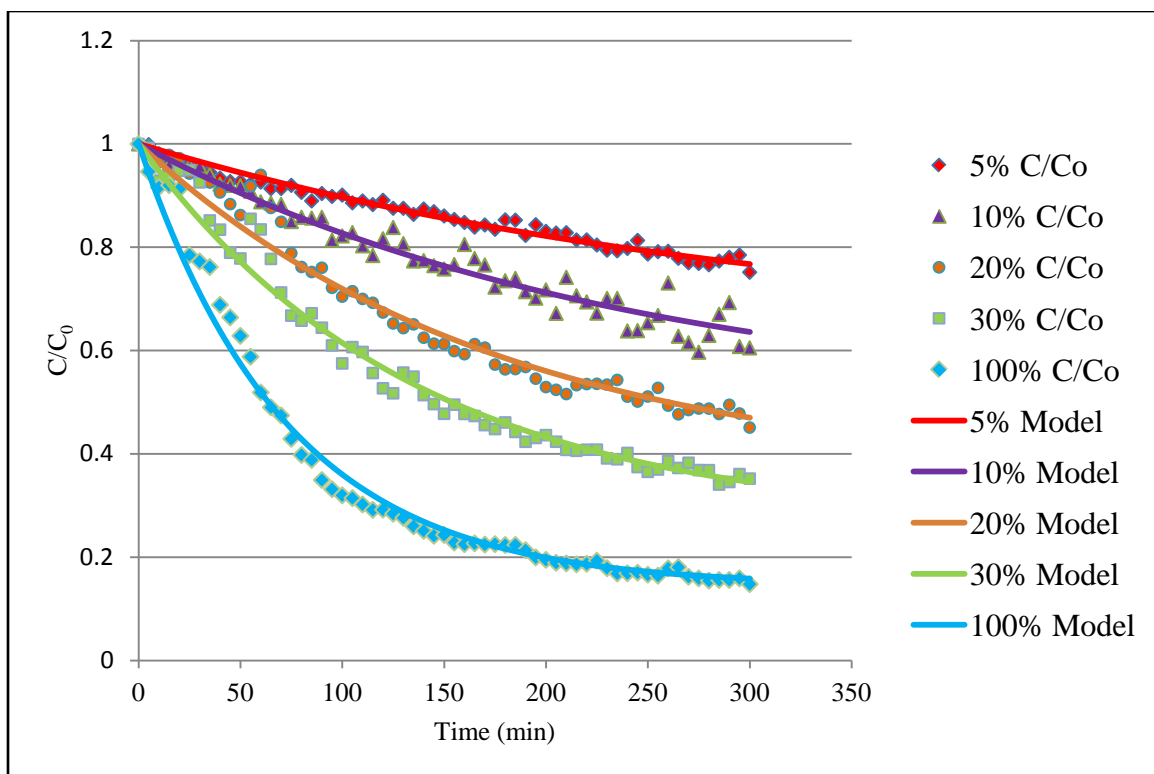


Figure 14 - Plotted concentration data for all duty cycles at 0.7ml/min flow rate

To address the investigative questions regarding the relative effectiveness of the differing duty cycle, the degradation rate constants (k_s) were normalized using Equation 7. The mean adjusted degradation rate constant ($k_{s \text{ adj}}$) for the 100% duty cycle (continuously on) was $0.0136 \text{ minute}^{-1}$, the mean adjusted degradation rate constant ($k_{s \text{ adj}}$) for the 30% duty cycle was $0.0176 \text{ minute}^{-1}$, the mean adjusted degradation rate constant ($k_{s \text{ adj}}$) for the 20% duty cycle was $0.0181 \text{ minute}^{-1}$, the mean adjusted degradation rate constant ($k_{s \text{ adj}}$) for the 10% duty cycle was $0.0225 \text{ minute}^{-1}$, and the mean adjusted degradation rate constant ($k_{s \text{ adj}}$) for the 5% duty cycle was $0.0281 \text{ minute}^{-1}$.

¹. [Figure 15](#) ~~Figure 15~~ plots these values along with standard error bars.

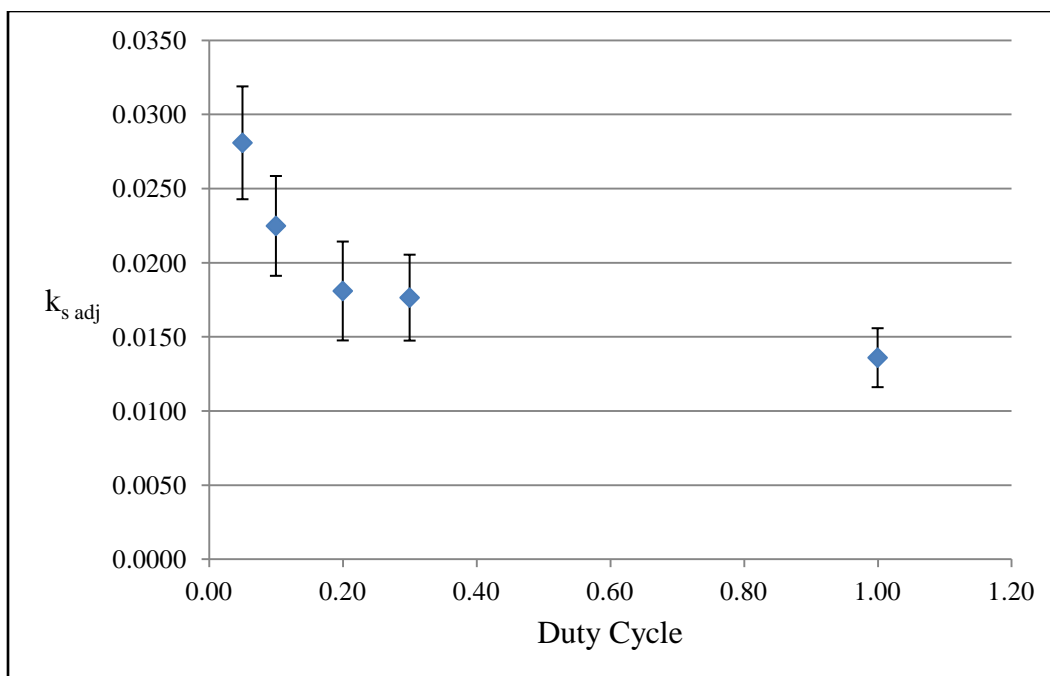


Figure 15 - Adjusted rate constants versus UV LED duty cycle showing standard error bars

A two-way ANOVA performed using JMP[®] 11 analytical software found the duty cycle to be a significant factor at $\alpha=0.05$ in relation to the adjusted degradation rate constant ($k_{s \text{ adj}}$). Flow rate and the interaction between flow rate and duty cycle were not significant. Tukey analysis of the significant effect of duty cycle showed the adjusted degradation rate constant ($k_{s \text{ adj}}$) for the 5% duty cycle to be significantly larger than the 20%, 30% and 100% duty cycles at $\alpha=0.05$ ($k_{s \text{ adj}}$ (5%) = 150% to 200% $k_{s \text{ adj}}$ (20%, 30%, 100%)). This analysis also showed the adjusted degradation rate constant ($k_{s \text{ adj}}$) for the 10% duty cycle to be significantly larger than the 100% duty cycle ($k_{s \text{ adj}}$ (10%) = 165% $k_{s \text{ adj}}$ (100%)). These values show that the differing duty cycles of the UV LEDs result in a different adjusted degradation rate constants ($k_{s \text{ adj}}$) for the Advanced Oxidation Process. The higher adjusted degradation rate constant ($k_{s \text{ adj}}$) observed at

lower duty cycles suggests a design parameter worth consideration in the design of future operational UV LED AOP systems.

Based on these data showing a higher adjusted degradation rate constants ($k_{s \text{ adj}}$) at the lower duty cycles, and additional round of duty cycle testing was performed. These additional experiments doubled the number of 11ms pulses of UV light in a 110ms period, and quadrupled the number of 5.5ms pulses. This would be equivalent to doubling the pulses used for the 10 percent duty cycle experiments, and consisted of a 20 percent duty cycle at 18.18Hz (11 milliseconds (ms) on, 44 ms off). The quadrupling of the 5.5ms pulses was achieved by using a 20 percent duty cycle at 36.36 Hz (5.5 milliseconds (ms) on, 22 ms off). Graphical representation of these duty cycles are shown in Figure 16 and can be compared to Figure 4. Based on the findings of Korovin et al. the adjusted degradation rate constants ($k_{s \text{ adj}}$) for these duty cycles was expected to be higher than for the initial 20 percent duty cycle due to the higher frequency (2015).

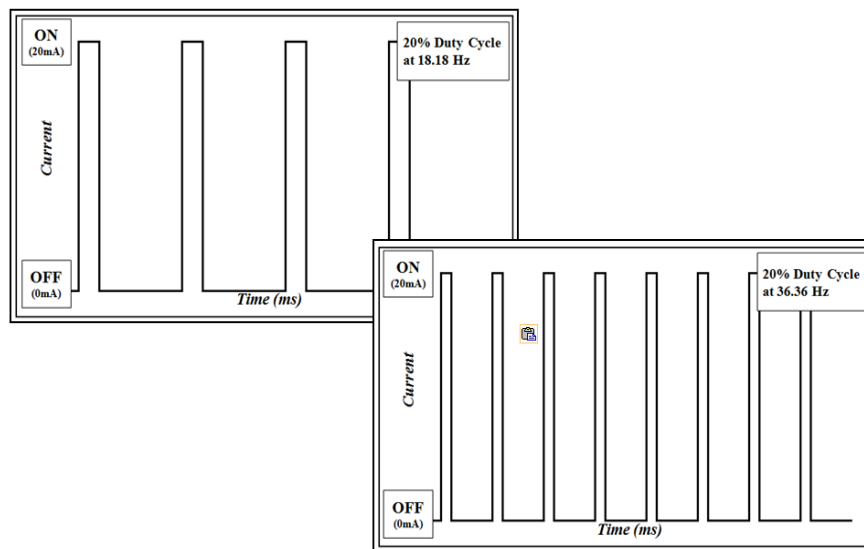


Figure 16 – Additional experimental duty cycles

The additional experimental duty cycles resulted in adjusted degradation rate constants ($k_{s \text{ adj}}$) that are within one standard deviation of all of the previous 20 percent duty cycle experiments. The plotted value is shown in Figure 17, and does not show any higher value due to the higher frequency. These results may indicate that the improved adjusted degradation rate constant ($k_{s \text{ adj}}$) values at the lower duty cycles may be attributable to the ration of dark time to UV exposure as posited by Sczechowski et al. (1993)

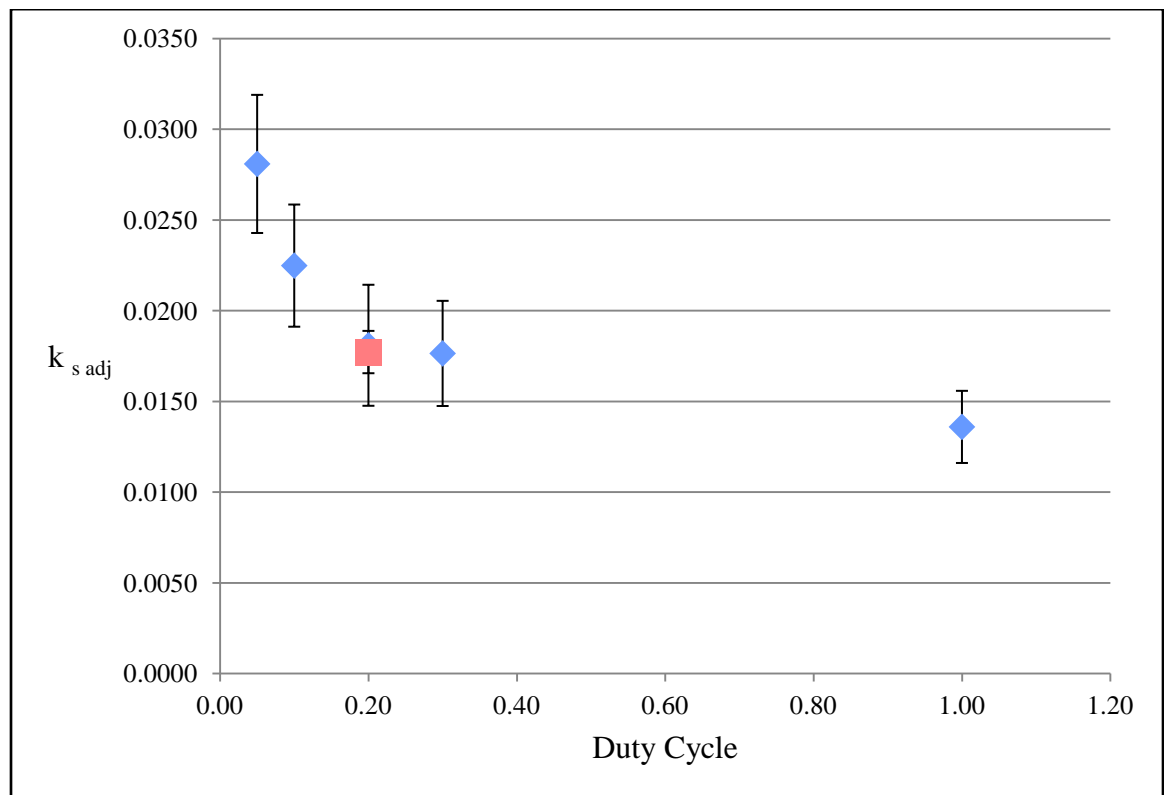


Figure 17 - Adjusted degradation rate constant ($k_{s \text{ adj}}$) for conditions in Figure 15 (indicated by diamonds) and the additional duty cycles (indicated by square).

Although not indicated to be a statistically significant factor in these analyses, the flow rate of the experimental solution through the reactor could emerge as a possible factor in further research where more numerous trials are conducted. As described, these

data are a result of experiments where each experimental flow rate condition was repeated twice with each of the five duty cycles. While the results proved sufficient to demonstrate a statistically significant relationship between duty cycle and the adjusted degradation rate constant ($k_{s \text{ adj}}$), the limited quantity of trials may have prevented a significant relationship between flow rate and the adjusted degradation rate constant ($k_{s \text{ adj}}$) from emerging. Examining the data graphed in Figure 18, it appears that the values for adjusted degradation rate constant ($k_{s \text{ adj}}$) relative to flow rate may separate as higher numbers of trials help to narrow the confidence intervals for the values of $k_{s \text{ adj}}$. Observing the separation of the two flow rates in the 20% to 30% region of the plotted data, it may be possible that the higher flow rate decreases the value of the adjusted degradation rate constant ($k_{s \text{ adj}}$).

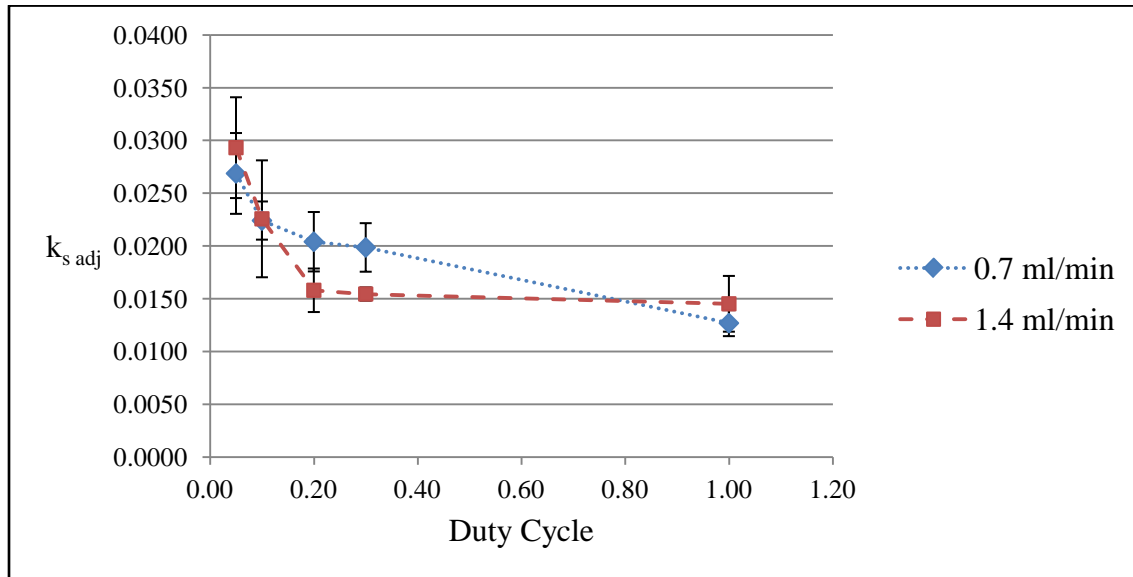


Figure 18 - Comparison of adjusted degradation rate constant ($k_{s \text{ adj}}$) by flow rate

Summary

The results and analysis presented address the investigative questions and contribute data toward answering the overarching research question of what operating parameters should be used with UV LEDs to most efficiently drive an AOP.

Measurements of post-experiment UV LEDs used in a methylene blue AOP reactor showed a mean reduction in total power transmission of 37%. Comparative testing of UV LEDs submerged in methylene blue and Brilliant Blue FCF for varying time periods indicated that the adsorption of Brilliant Blue FCF onto the lenses of the UV LEDs was less than the adsorption of methylene blue by a statistically significant margin. Time of submersion did not show a statistically significant effect. Control experiments showed Brilliant Blue FCF to be stable in the presence of UV light and H_2O_2 independently and was thus suited for use as a witness dye in AOP experiments. Varying the duty cycle of the UV LEDs showed a significant effect on the adjusted degradation rate constant ($k_{s \text{ adj}}$) for AOP reactions.

V. Conclusions and Recommendations

This research demonstrated the effectiveness of UV LEDs in driving an AOP. The results also confirmed Brilliant Blue FCF as a suitable witness dye for evaluation of AOP reaction rates. The observed effect of the lowest duty cycle yielding the greatest adjusted rate constant may prove useful in the future employment of UV LEDs in AOPs. These findings are of use for future research and possible development of UV LED driven AOP decontamination systems.

Conclusions and Significance of Research

While Brilliant Blue FCF had been shown as a suitable witness dye for decomposition by ozone (Handa, Minamitani and Higashiyama 2007), these experiments show that it is also suitable for use in UV/H₂O₂ AOPs. Control experiments demonstrated little to no degradation of Brilliant Blue FCF in the presence of solely UV light, or solely H₂O₂. Brilliant Blue FCF also demonstrated less adsorption onto the quartz UV LED lenses than the methylene blue used in preceding experiments. In addition to these positive attributes, Brilliant Blue FCF degraded well in an AOP. Compared to the tartrazine dye used in parallel research, Brilliant Blue FCF degraded at a much more rapidly, yielding degradation rate constants eight to fifteen times greater (Mudimbi 2015). Brilliant Blue FCF also yielded rate constants 50-100% higher than achieved with the same duty cycles using methylene blue (Duckworth, et al. In Review). These differences could be due to the decomposition of Brilliant Blue FCF molecule yielding fewer, or less reactive byproducts during the AOP, allowing the hydroxyl radicals to more fully contribute to the decolorization of the dye.

Brilliant Blue FCF demonstrated less adsorption onto the lenses of the UV LEDs in both the immersion experiment, and also regression analysis of the adjusted rate constants over the course of the experimental trials. The immersion experiments showed that the adsorption of both methylene blue, and Brilliant Blue FCF onto the quartz UV LED lenses did not differ with time. This behavior differs from the linear regression analysis of the sets of UV LEDs used in both the methylene blue and Brilliant Blue FCF reactors, which both showed a decrease in adjusted degradation rate constants throughout the approximately 100 hours required for each experiment (the decrease being two to three times less for Brilliant Blue FCF). This difference in the relationship between time and perceived reduction in transmission could be attributable to the LEDs in the reactors being powered. The powered LED could have different behavior than the submersed LEDs due to differences in temperature, charge, and contact with hydroxyl radicals and AOP by products. The presence of an electrical current in the LED may change the charge of the lens and increase its adsorptive properties with relation to time. Additionally, the increased temperature due to the activation of the LED, may make the LED lenses more adsorptive of the dye, or the dye AOP byproducts (which are not present in the immersion test).

The significantly higher adjusted degradation rate constant for the lowest duty cycle represents a potentially useful driving parameter for UV LEDs in AOPs. This behavior indicates that low duty cycle pulsed UV is more efficient at driving the UV/H₂O₂ AOP than higher duty cycles and constant on (100% duty cycle). Other research on the effects of pulsed UV, also called controlled periodic illumination, on photocatalytic reactions also found higher efficiency at the lowest duty cycles

(Korovin, et al. 2015). The data gathered on adjusted degradation rate constant ($k_{s\text{ adj}}$) indicates an inverse relationship with duty cycle. As duty cycle decreased the adjusted degradation rate constant ($k_{s\text{ adj}}$) increased, and expressed a maximum value at the minimum duty cycle (5%). Analysis of similar attributes of higher quantum efficiency in photocatalytic reactions attribute the effect to the continued reaction of the radicals created by UV light during the dark period (Korovin, et al. 2015). Research indicates the effect of controlled periodic illumination is related to the lifespan of the active species of radicals created in the reaction (Korovin, et al. 2015) (Szczechowski, Koval and Noble 1993) .

Recommendations for Future Research

Numerous opportunities exist for further research into the use of UV LEDs in Advanced Oxidation Processes. These Include:

1.) Development of a scalable flow through reactor design.

While effective for research, the reactor design used to collect data does not represent a design that could be effectively upscaled to address moderate or large scale water decontamination through an AOP and in some trials yielded un-attributable noise in the data. Designing a flow through reactor that uses a pipe, sheet flow, or weir type structure as the reactor vessel should provide a structure that is more scalable, and offer a more predictable flow pattern.

Based on the demonstrated effectiveness of pulsing, and the intermittent application of UV light energy, the reactor may not need to be of a design where the solution is always in contact with UV light. In addition to the

possibility of pulsing the UV LEDs to create controlled periodic illumination, the reactor could use a fixed array of UV LEDs and vary UV exposure by increasing or decreasing the flow rate. Conversely, the reactor could use a large array of UV LEDs, and only activate those necessary to reach the desired reaction level.

- 2.) Investigate the possible relationship between flow rate and adjusted degradation rate constant.

As discussed in the presentation of the results, a relationship between flow rate and adjusted degradation rate constant may have emerged with more data points. More extensive testing, including more experimental trials, and more experimental flow rates would help to determine if a relationship between flow rate and adjusted degradation rate constant exists. This could include flow rates greater and less than the 0.7 ml/min and 1.4 ml/min used in these experimental trials.

- 3.) Further testing of UV LEDs to determine UV LED characteristics.

This research executed testing with only a single type of UV LED due to limited availability. Further evaluation of UV LEDs as more sources come on line, and as more manufacturing methods are developed for UV LED substrates could be valuable. These evaluations could focus on various characteristics including LED lifespan with respect to on-off cycles and heating.

Summary

Through data generated through experimentation, this research demonstrated the effectiveness of UV LEDs in driving an AOP. In the course of these experiments, Brilliant Blue FCF was confirmed as a suitable witness dye for evaluation of AOP reaction rates. Evaluation of the effect of duty cycle found the lowest duty cycle yielded the greatest adjusted degradation rate constant. This information may prove useful in the future employment of UV LEDs in AOPs and possible development of UV LED driven AOP decontamination systems.

Appendix A - UV LED Experimental Condition Setup Procedures

Assemble and Mix Experimental Solution: 5-millimolar (mM) hydrogen peroxide and 0.01-millimolar (mM) Brilliant Blue FCF

In 1 liter volumetric flask:

Using a pipette and a 10 ml graduated cylinder, measure out 5ml of 2.0mM Brilliant Blue FCF Stock Solution

Transfer 5 ml of stock solution to the volumetric flask

Use deionized water to rinse remaining stock solution out of the graduated and into the 1 liter volumetric flask

Weigh out 0.5669g of grams hydrogen peroxide (30% in water) in weighing tray

Transfer 0.5669g of grams hydrogen peroxide to volumetric flask, rinsing entire contents of the weighing tray into the 1 liter volumetric flask

Record exact quantity of H_2O_2 in solution

Fill remainder of flask with reverse osmosis deionized water up to the 1 liter mark

Drop in stir bar and place on stir plate while you set up the driver board and reactor.

Set Up Driver-board and Wire Board to Reactor LEDs:

Disconnect board from power to prevent voltage spikes in LEDs or inadvertently energizing the circuit.

Follow Numbered sequence and connect LEDs to board (1 on Top, to 7 on the bottom)

Set Up LED Drive Pattern:

Turn on DasyLab computer

Ensure computer is connected to blue driver box by USB Cable

Open DasyLab software (can select drive pattern program from desktop shortcuts)

Ensure power supply to driver board is plugged in

Press play button on DasyLab GUI

Use oscilloscope to verify duty cycle at output terminals of driver box (should see proper on-off pattern, squared waves, and proper magnitude)

Use oscilloscope to verify duty cycle across resistors for all 7 LED circuits on the driver board.

Check voltage and current using a multimeter

Disconnect power source to de-energize LEDs for remainder of experiment set-up

Set Up Cary-60 UV-Vis Spectrophotometer:

Log on to desktop computer:

Username: Cary60

No password

Open “Cary60” program

Open “Scan” file

Zero instrument:

Fill flow through cuvette with deionized water using a syringe (ensure no bubbles are in cuvette)

Open dark panel in left side of UV Vis Spectrophotometer

Load flow through cuvette containing water into the instrument

Close the panel

Click “Zero”

Retrieve solution from the stir plate.

Make Calibration Samples (0%, 25%, 50%, 75%, 100%)

Using a syringe for the experimental solution, and a squirt bottle filled deionized water:

Fill 0% Calibration Sample w/ D.I. Water – Seal and shake to combine

Fill 25% Calibration Sample with 2.5mL of solution and add water to the 10mL mark – Seal and shake to combine

Fill 50% Calibration Sample with 5mL of solution and add water to the 10mL mark– Seal and shake to combine

Fill 75% Calibration Sample with 7.5mL of solution and add water to the 10mL mark– Seal and shake to combine

Fill 100% Calibration Sample with 10mL of solution– Seal and shake to combine

Use Cary-60 UV-Vis Spectrophotometer to Collect Values for Calibration Curve:

Thoroughly rinse syringe and shake dry.

Set measurement wavelength to 630nm for Brilliant Blue FCF

Use syringe to load flow cuvette through with 0% solution

Open panel, load cuvette into Cary-60 UV-Vis, and close panel

Scan & Record Cary-60 UV-Vis Reading for 0% solution

Use syringe to load flow cuvette through with 25% solution

Open panel, load cuvette into Cary-60 UV-Vis, and close panel

Scan & record Cary-60 UV-Vis Reading for 25% solution

Use syringe to load flow cuvette through with 50% solution

Open panel, load cuvette into Cary-60 UV-Vis, and close panel

Scan & record Cary-60 UV-Vis Reading for 50% solution

Use syringe to load flow cuvette through with 75% solution

Open panel, load cuvette into Cary-60 UV-Vis, and close panel

Scan & record Cary-60 UV-Vis Reading for 75% solution

Use syringe to load flow cuvette through with 100% solution

Open panel, load cuvette into Cary-60 UV-Vis, and close panel

Scan & record Cary-60 UV-Vis Reading for 100% solution

Set Up Fluid Flow Through Drive Console:

Empty water from reactor and purge all the lines with a syringe full of air.

Use syringe to prime inflow, outflow and flow through cuvette tubing lines with 100% solution.

Run inflow tubing through peristaltic pump, place inflow plug into the bottom of the reactor, and lock tubing into pump.

Fill the reactor to the top with 100% solution

Set up 100% solution inflow vessel and place inlet end of tubing in solution (make sure the end of the tube will stay in the bottom of the solution for the entire experiment)

Place outflow plug/line into the top of the reactor and load flow through cuvette into Cary-60 UV-Vis system (closing the shutter and covering the tubing gap with a dark cover)

Turn on pump

Check system for any leaks.

Set Up Proper Flow Rate

Using a stopwatch and a graduated cylinder calibrate pump speed to desired flow rate using the outflow line

Once flow rate is correct, place outflow line into waste collection vessel

Complete Experimental Set Up

On Cary-60 UV-Vis

Click “Command”

Click “Rapid Results”

Continue to take samples every few minutes until the absorption stabilizes

Setup automated data collection on Cary-60

Click “Setup”

Set start to “635” nm and stop to “625” nm (for 630 nm Brilliant Blue FCF Peak)

Check “cycle mode”

Set cycle count to “66” and cycle time to “5” min *Note: This means 66 readings will be taken in 5 minute intervals, subject to change depending on the experiment.

Select “fast”

Click “OK”

Plug in LED Driver Board and use oscilloscope to verify duty cycle at output terminals of driver box (should see proper on-off pattern, squared waves, and proper magnitude)

Click “start” when ready to start experiment data collection

*****EXPERIMENT RUNS*****

Shut down LEDs by stopping DasyLab and unplugging the driver board.

Stop pump.

Empty reactor, purge lines and flow through cuvette with syringe of deionized water and fill reactor with water to prevent dye from drying on LEDs

Pump water through the system to ensure it is completely filled.

Wash all syringes and mixing vessels and set aside to dry

When experiment is complete:

Click “save as”, name file, and click “save”

Click “save as” again, change file type to “.CSV”, and click “save”

Export data to another computer for data analysis

Cut out row for peak wavelength absorption vs. time (630nm for Brilliant Blue FCF)

Paste (transposed) into column into excel template

Input 0%, 25%, 50%, 75%, 100% calibration values into excel template

Use solver to adjust rate constant to minimize sum of squares difference between collected data and model line

Appendix B – Graphical Presentation of Data

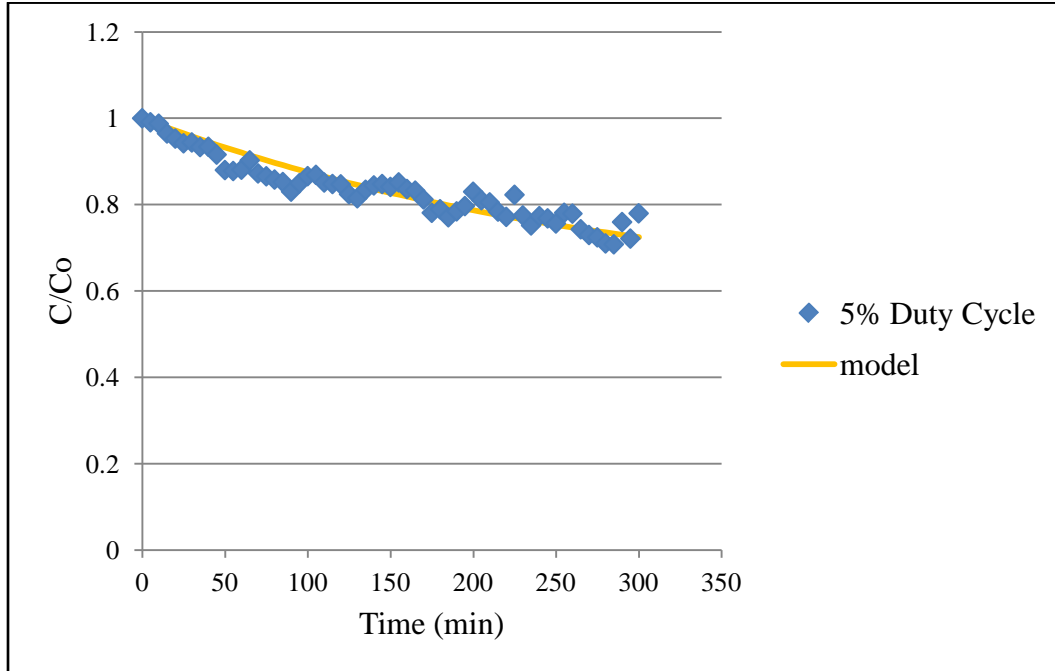


Figure 19 - 1st Test Cycle, 5% Duty Cycle, at 0.7 ml Flow Rate, $k_s = 0.00148$, Model-to-Data $R^2 = 0.91$

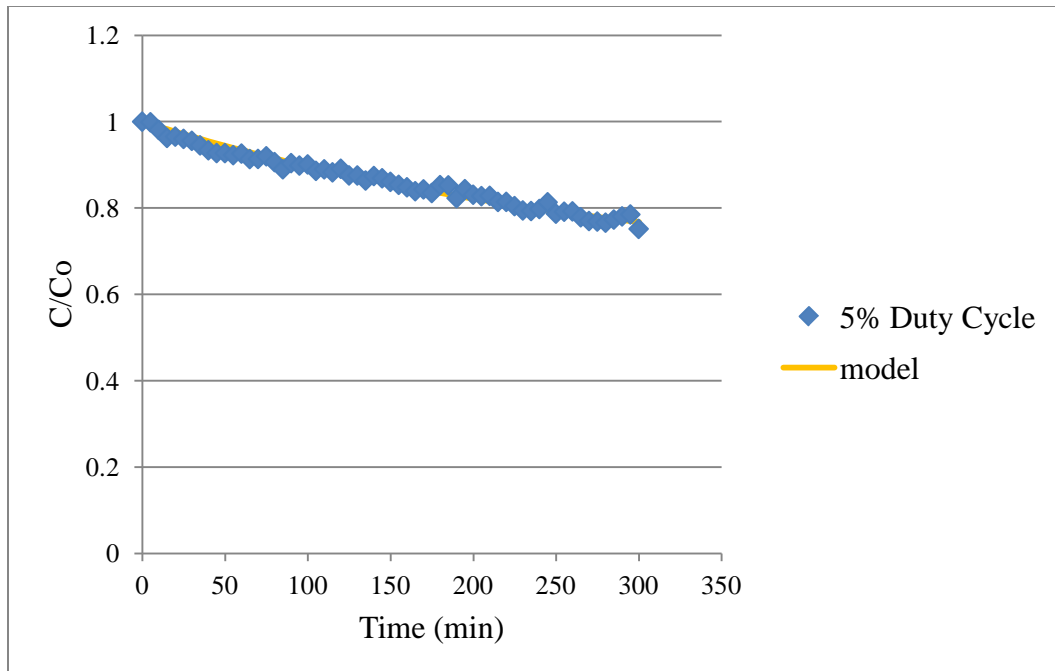


Figure 20 - 2nd Test Cycle, 5% Duty Cycle, at 0.7 ml Flow Rate, $k_s = 0.00121$, Model-to-Data $R^2 = 0.98$

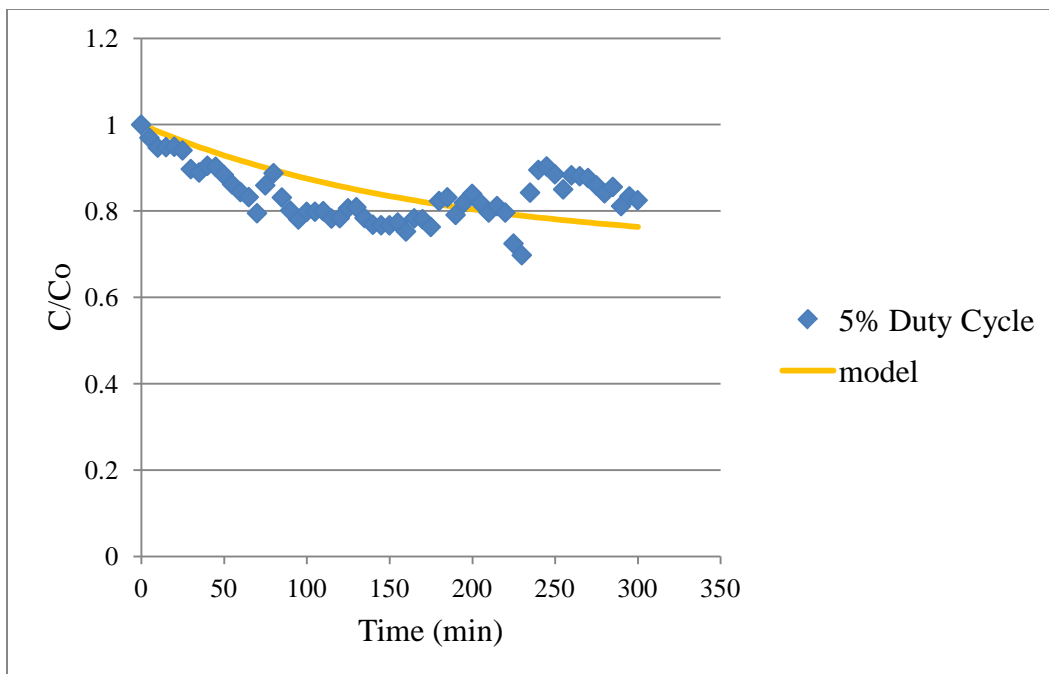


Figure 21 - 1st Test Cycle, 5% Duty Cycle, at 1.4 ml Flow Rate, $k_s = 0.00163$, Model-to-Data $R^2 = 0.28$

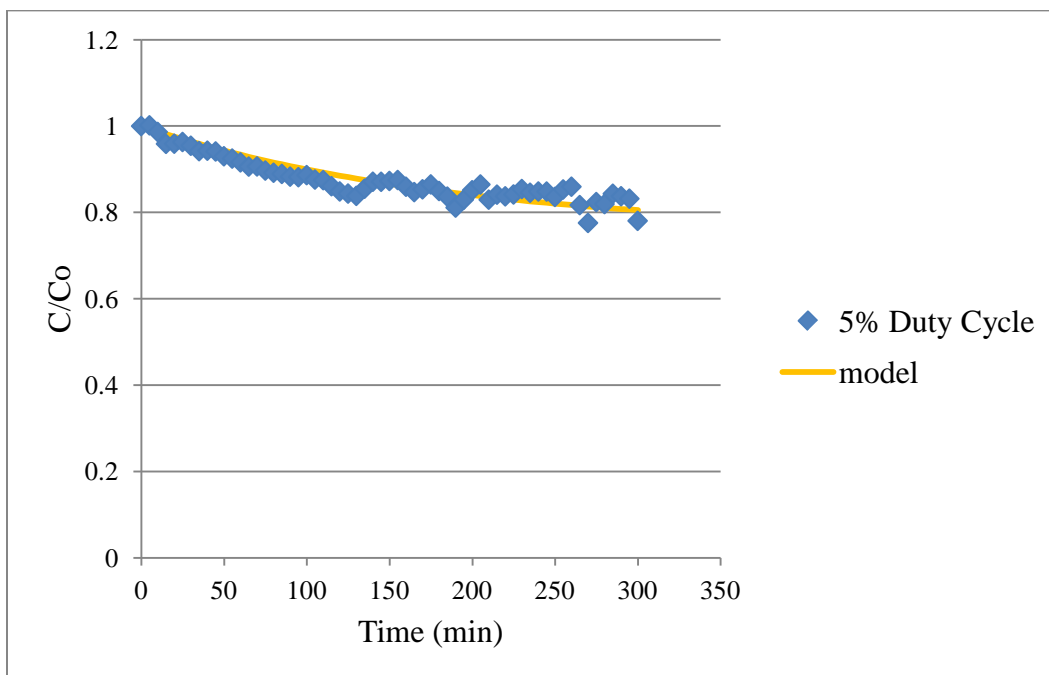


Figure 22 - 2nd Test Cycle, 5% Duty Cycle, at 1.4 ml Flow Rate, $k_s = 0.00130$, Model-to-Data $R^2 = 0.87$

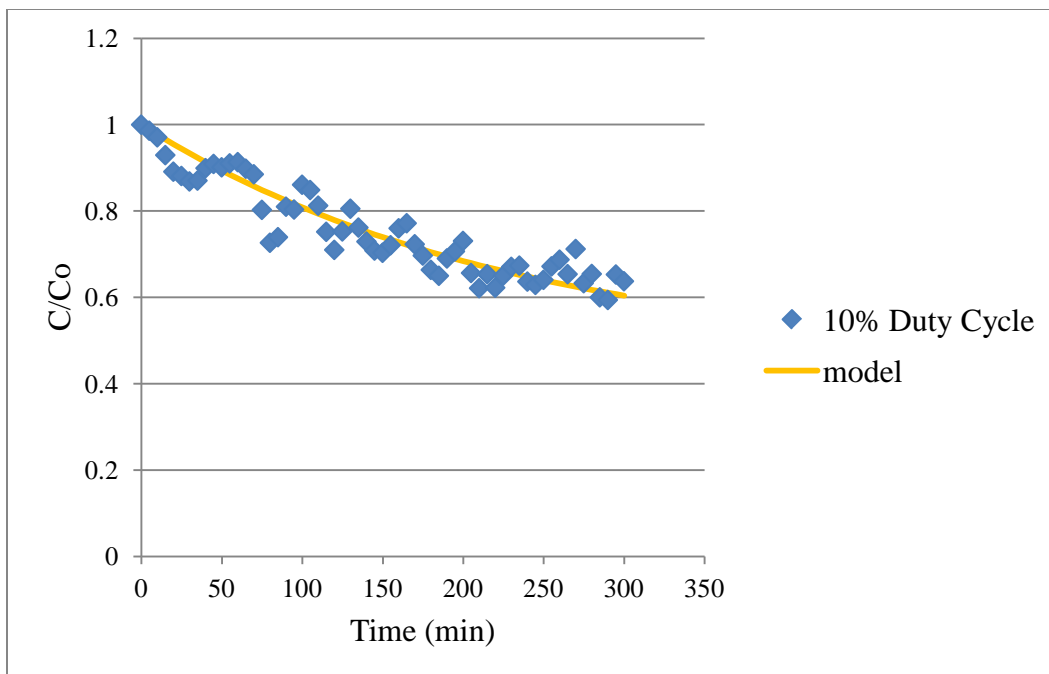


Figure 23 - 1st Test Cycle, 10% Duty Cycle, at 0.7 ml Flow Rate, $k_s = 0.00237$, Model-to-Data $R^2 = 0.88$

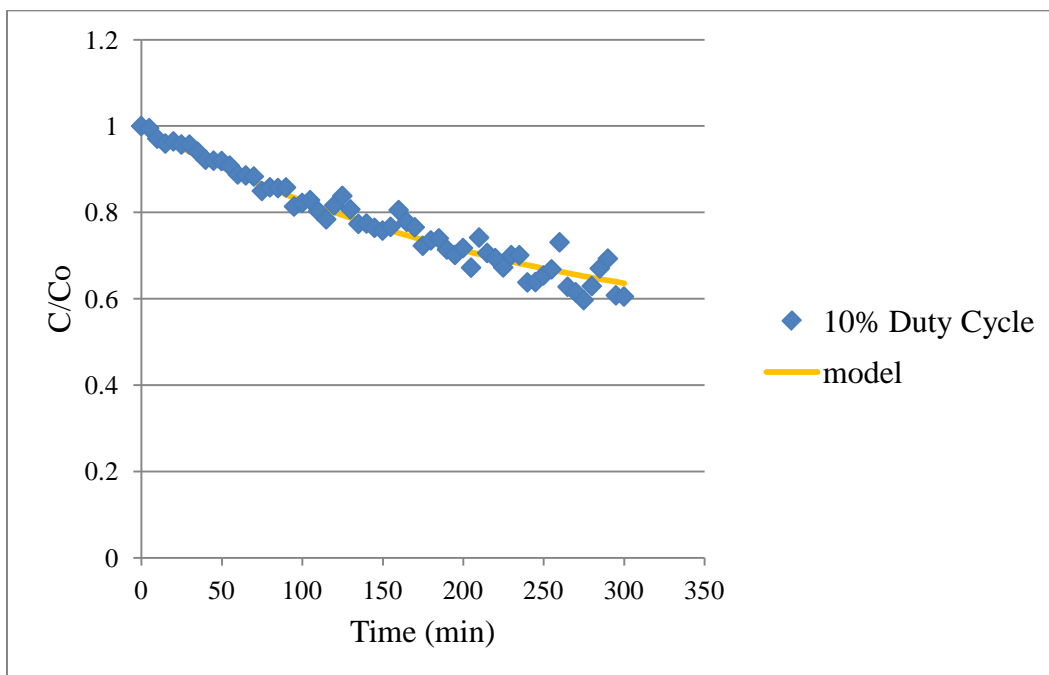


Figure 24 - 2nd Test Cycle, 10% Duty Cycle, at 0.7 ml Flow Rate, $k_s = 0.00211$, Model-to-Data $R^2 = 0.96$

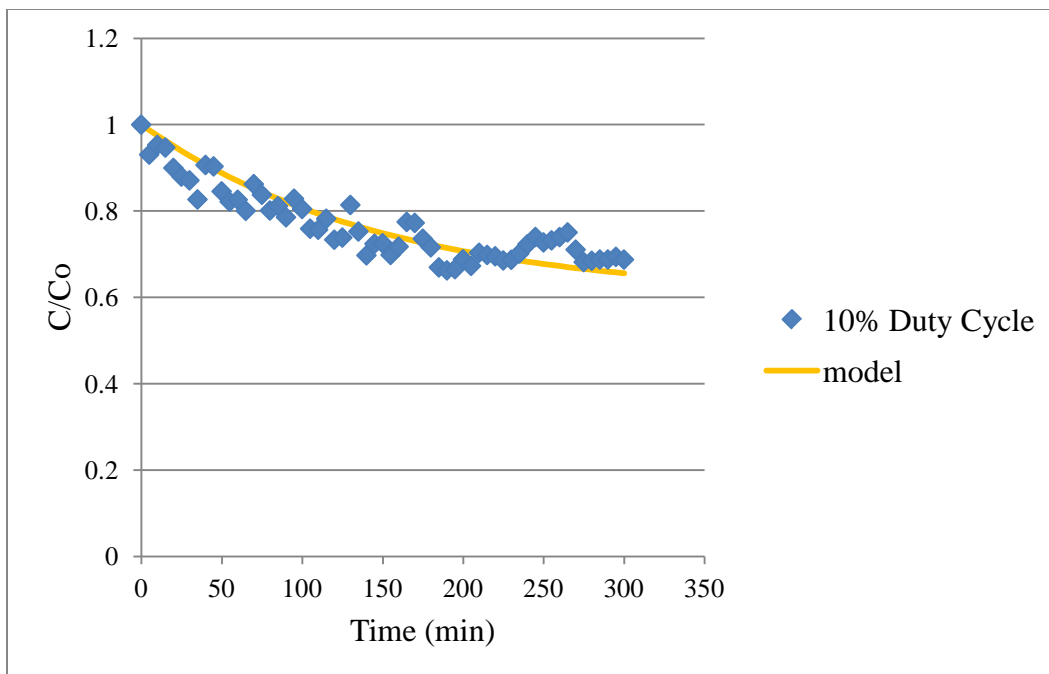


Figure 25 - 1st Test Cycle, 10% Duty Cycle, at 1.4 ml Flow Rate, $k_s = 0.00265$, Model-to-Data $R^2 = 0.86$

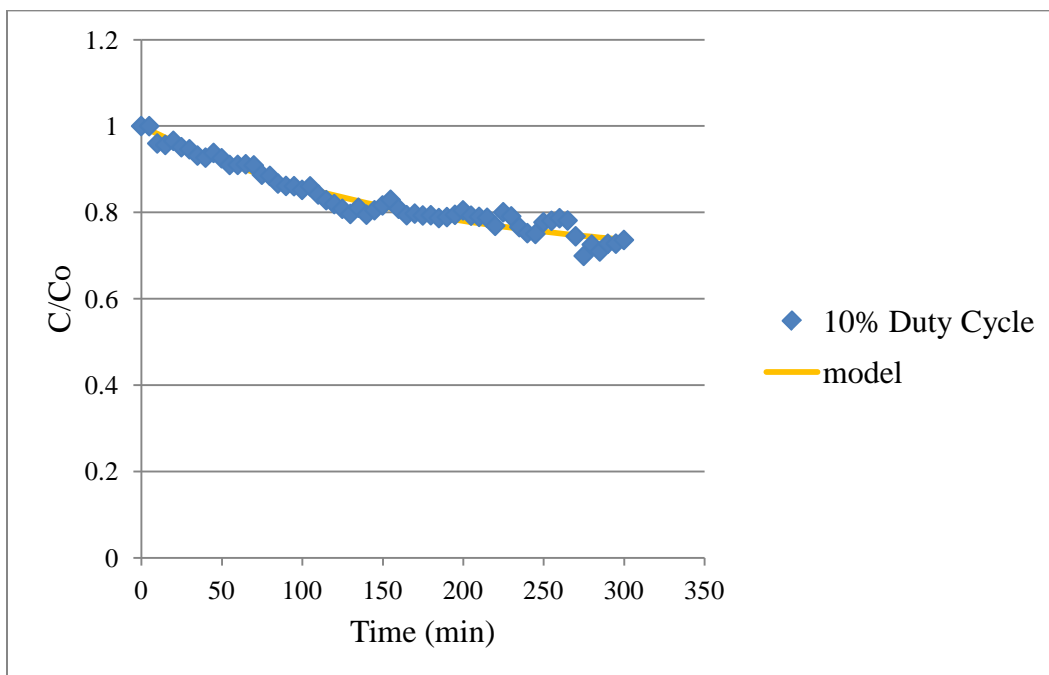


Figure 26 - 2nd Test Cycle, 10% Duty Cycle, at 1.4 ml Flow Rate, $k_s = 0.00186$, Model-to-Data $R^2 = 0.95$

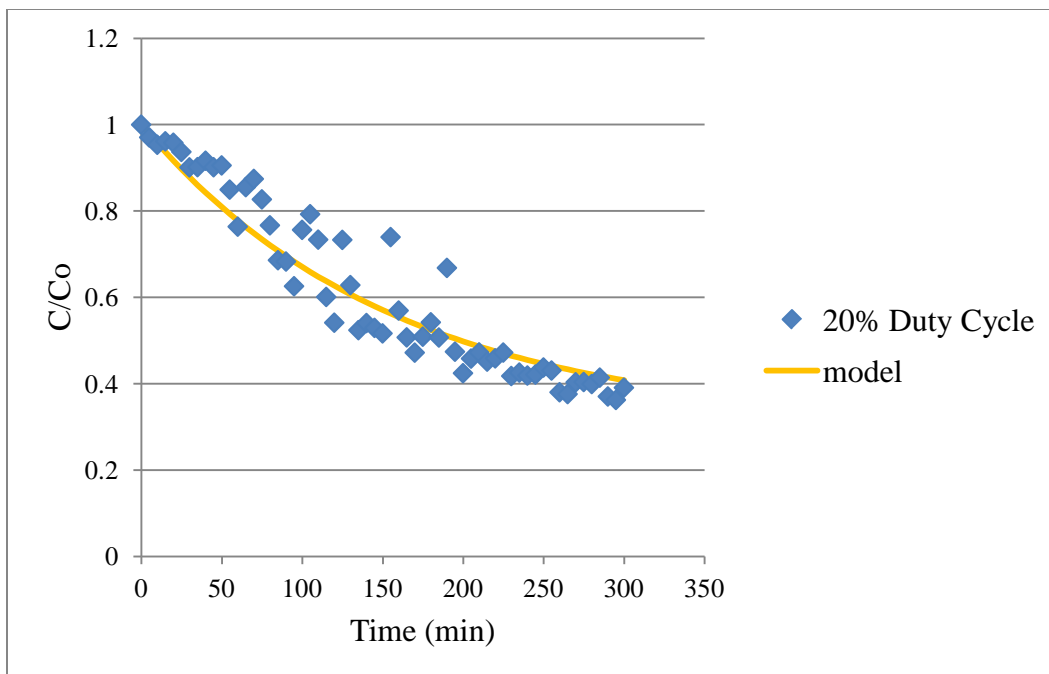


Figure 27 - 1st Test Cycle, 20% Duty Cycle, at 0.7 ml Flow Rate, $k_s = 0.00448$, Model-to-Data $R^2 = 0.92$

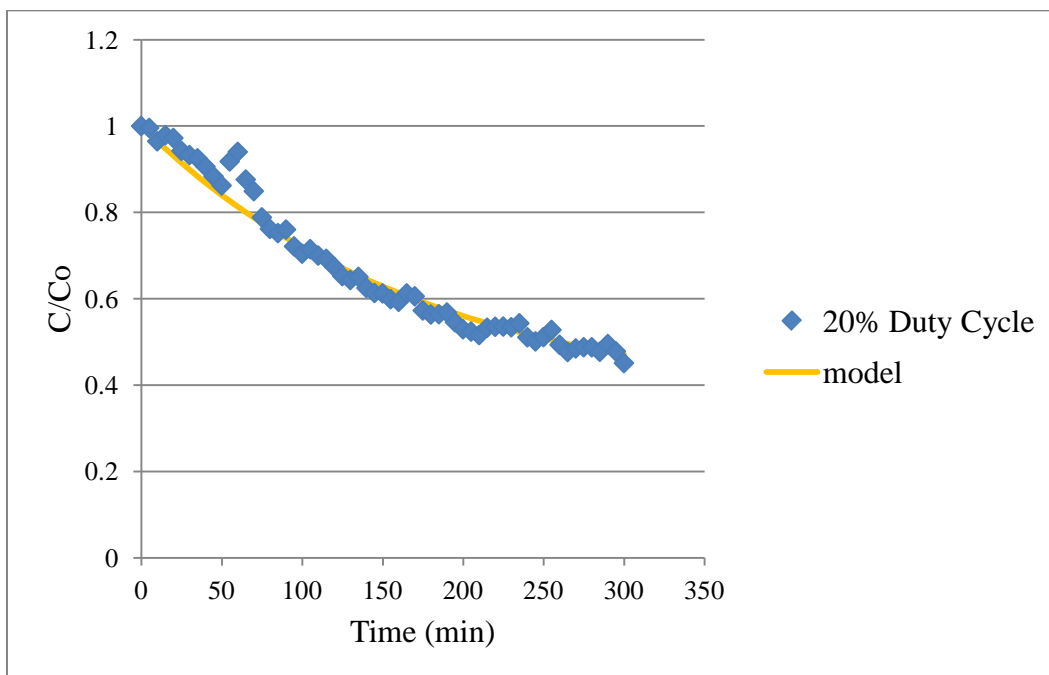


Figure 28 - 2nd Test Cycle, 20% Duty Cycle, at 0.7 ml Flow Rate, $k_s = 0.00368$, Model-to-Data $R^2 = 0.98$

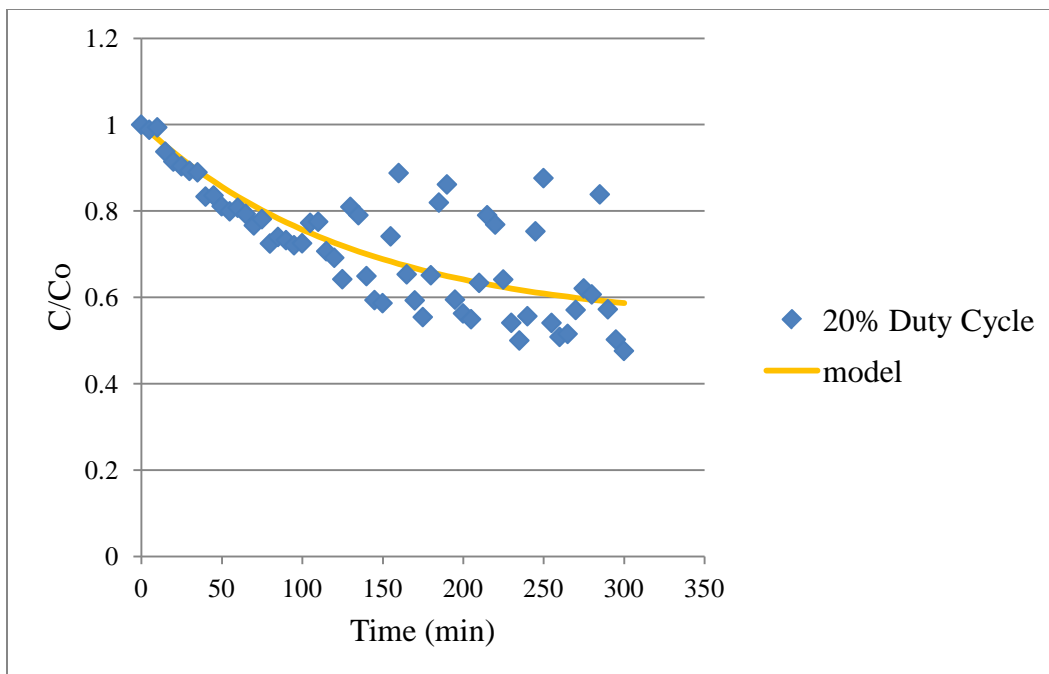


Figure 29 - 1st Test Cycle, 20% Duty Cycle, at 1.4 ml Flow Rate, $k_s = 0.00345$, Model-to-Data $R^2 = 0.59$

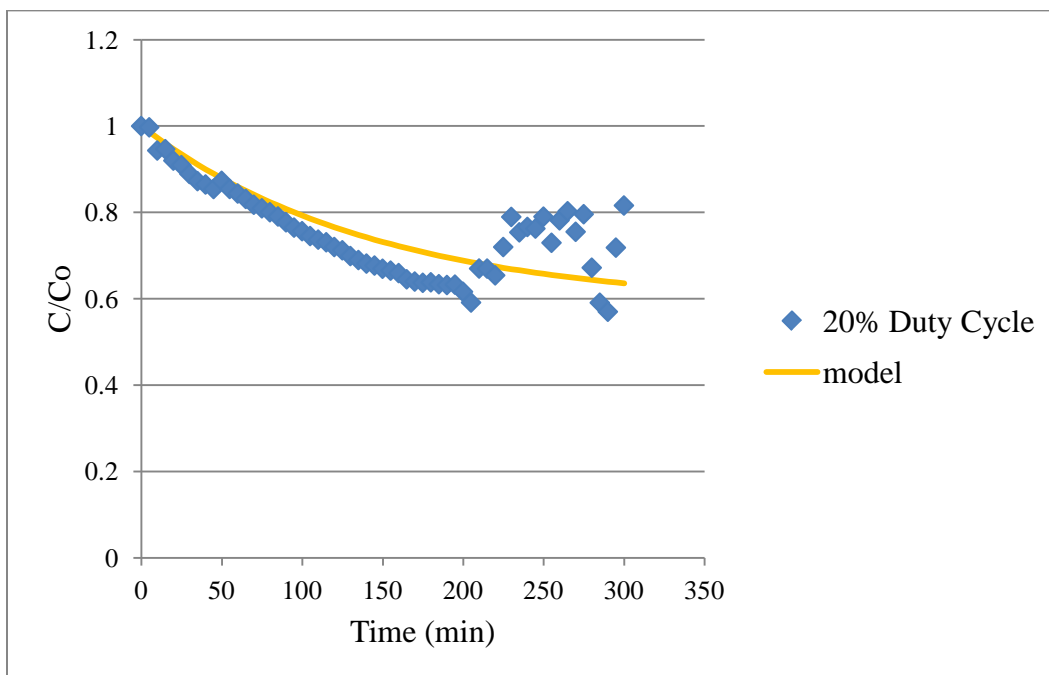


Figure 30 - 2nd Test Cycle, 20% Duty Cycle, at 1.4 ml Flow Rate, $k_s = 0.00287$, Model-to-Data $R^2 = 0.61$

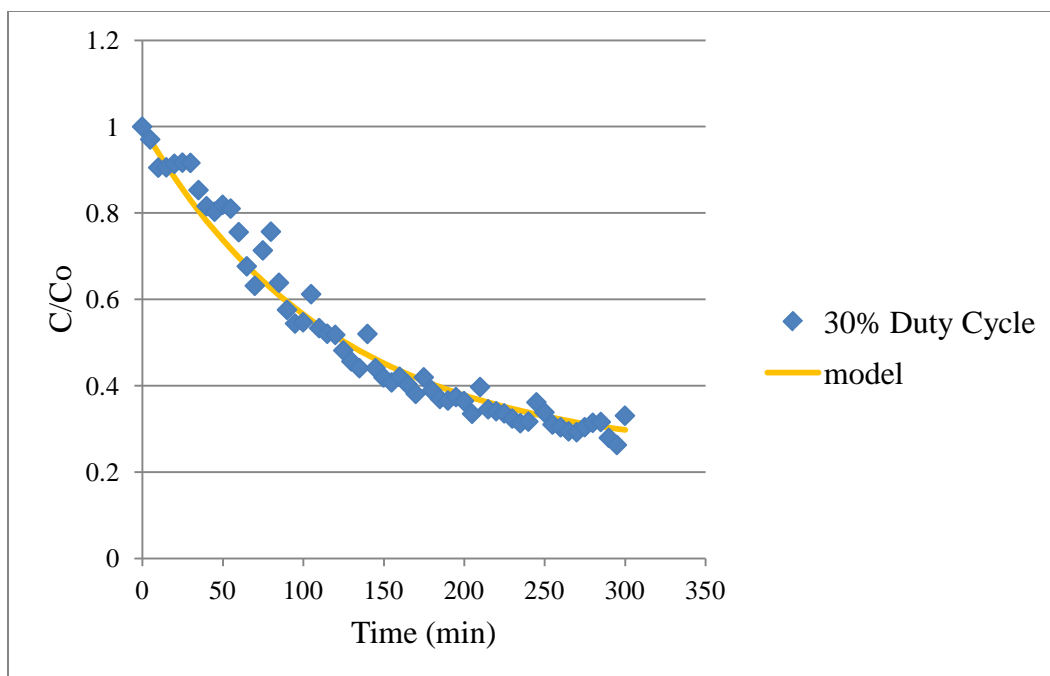


Figure 31 - 1st Test Cycle, 30% Duty Cycle, at 0.7 ml Flow Rate, $k_s = 0.00644$, Model-to-Data $R^2 = 0.97$

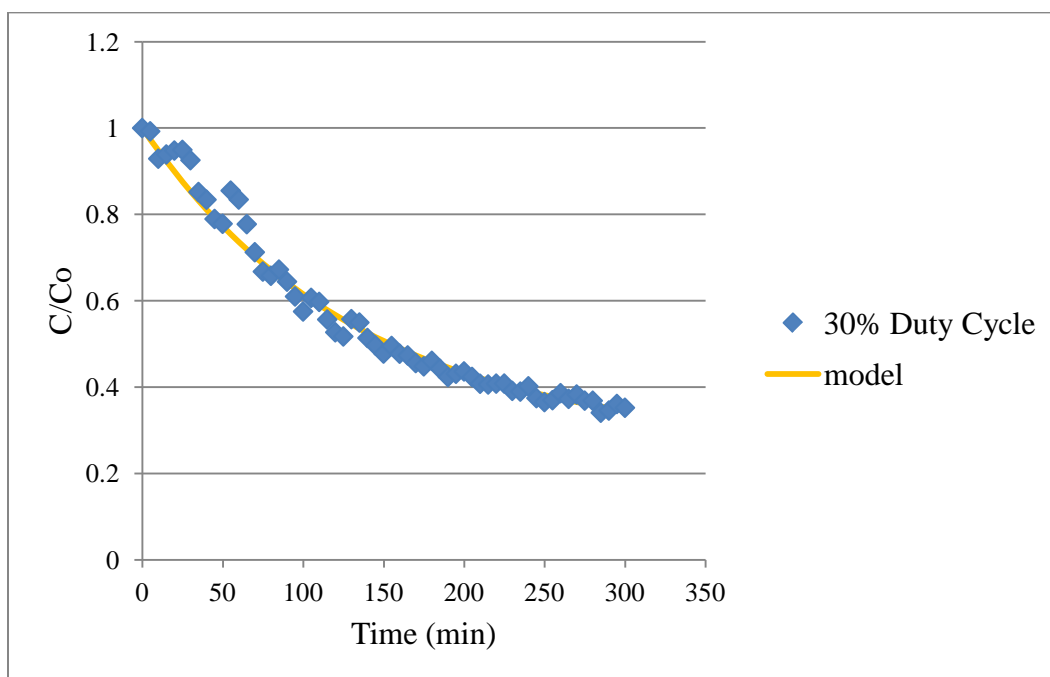


Figure 32 - 2nd Test Cycle, 30% Duty Cycle, at 0.7 ml Flow Rate, $k_s = 0.00546$, Model-to-Data $R^2 = 0.98$

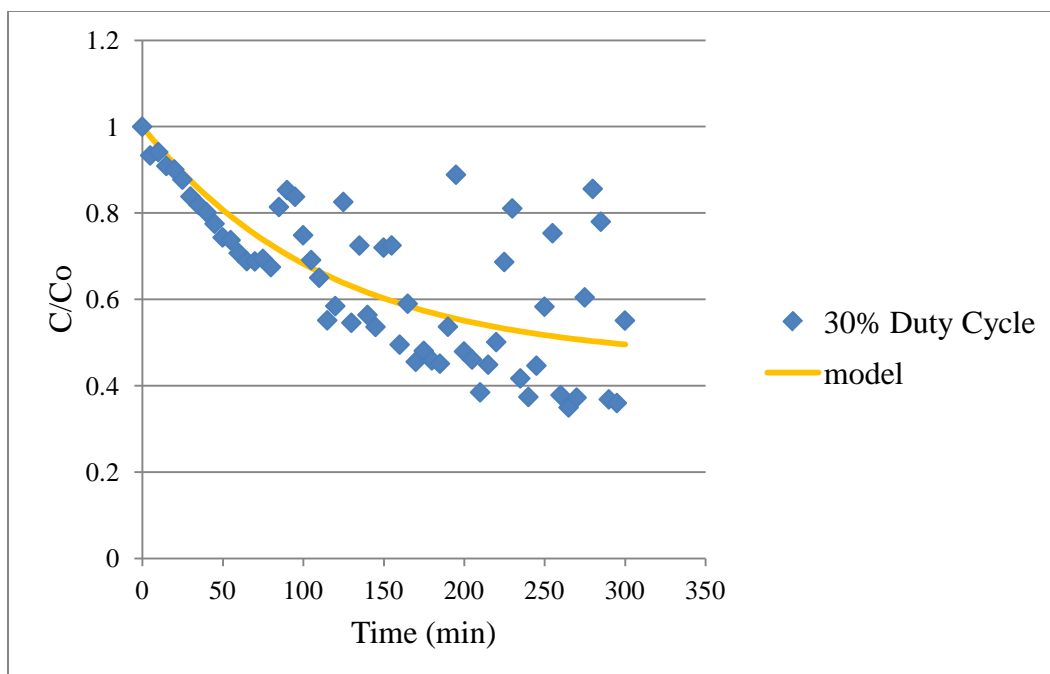


Figure 33 - 1st Test Cycle, 30% Duty Cycle, at 1.4 ml Flow Rate, $k_s = 0.00476$, Model-to-Data $R^2 = 0.52$

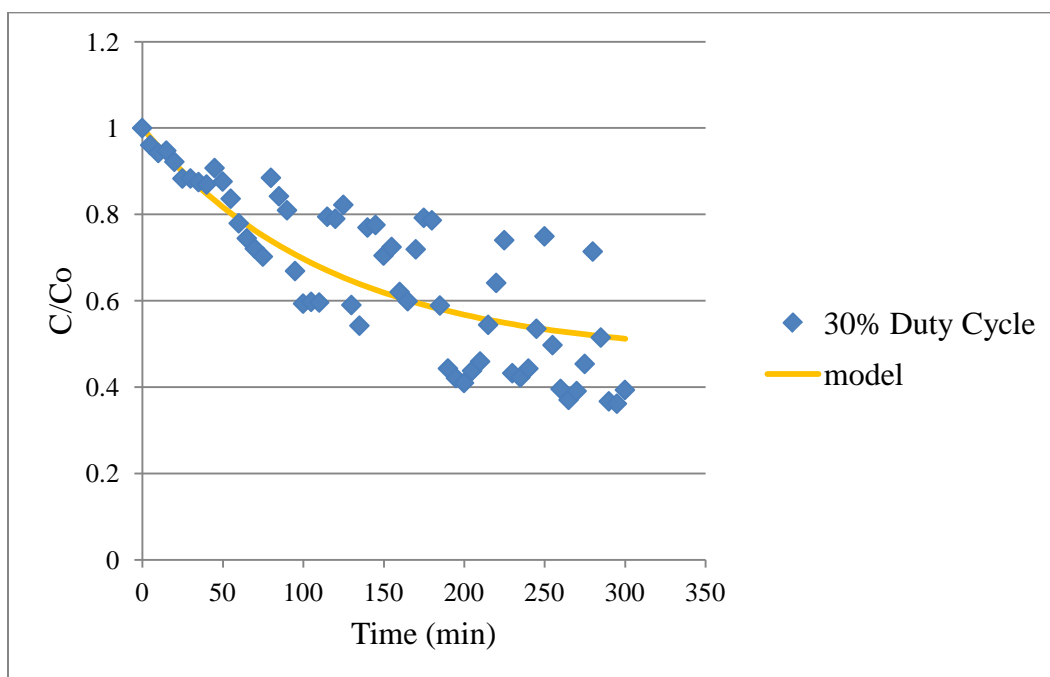


Figure 34 - 2nd Test Cycle, 30% Duty Cycle, at 1.4 ml Flow Rate, $k_s = 0.00450$, Model-to-Data $R^2 = 0.67$

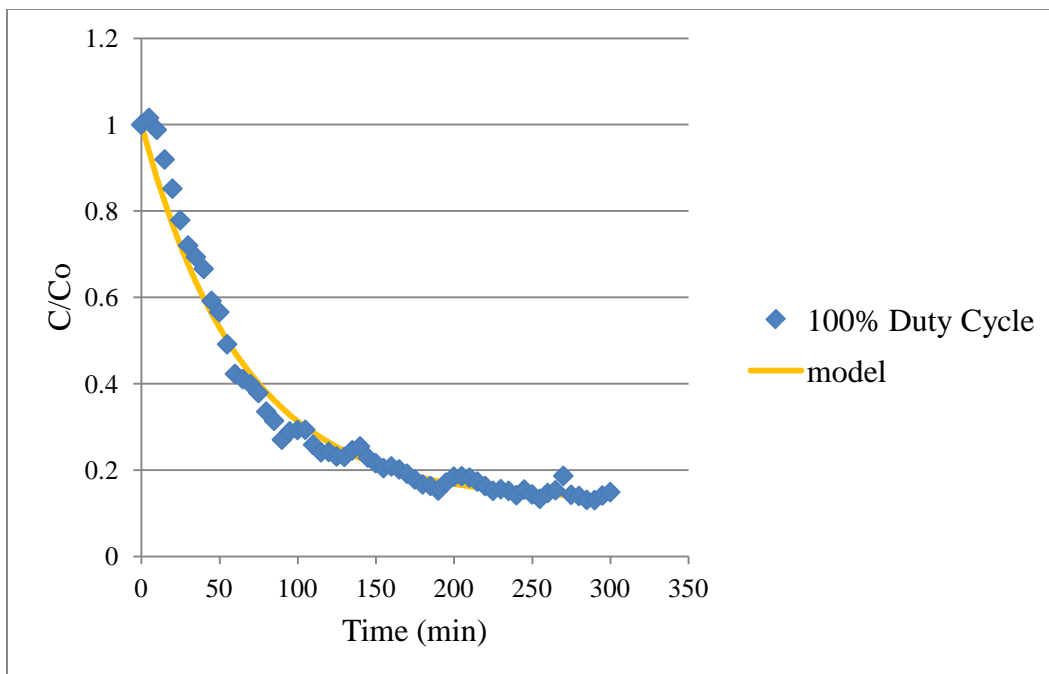


Figure 35 - 1st Test Cycle, 100% Duty Cycle, at 0.7 ml Flow Rate, $k_s = 0.01355$, Model-to-Data $R^2 = 0.99$

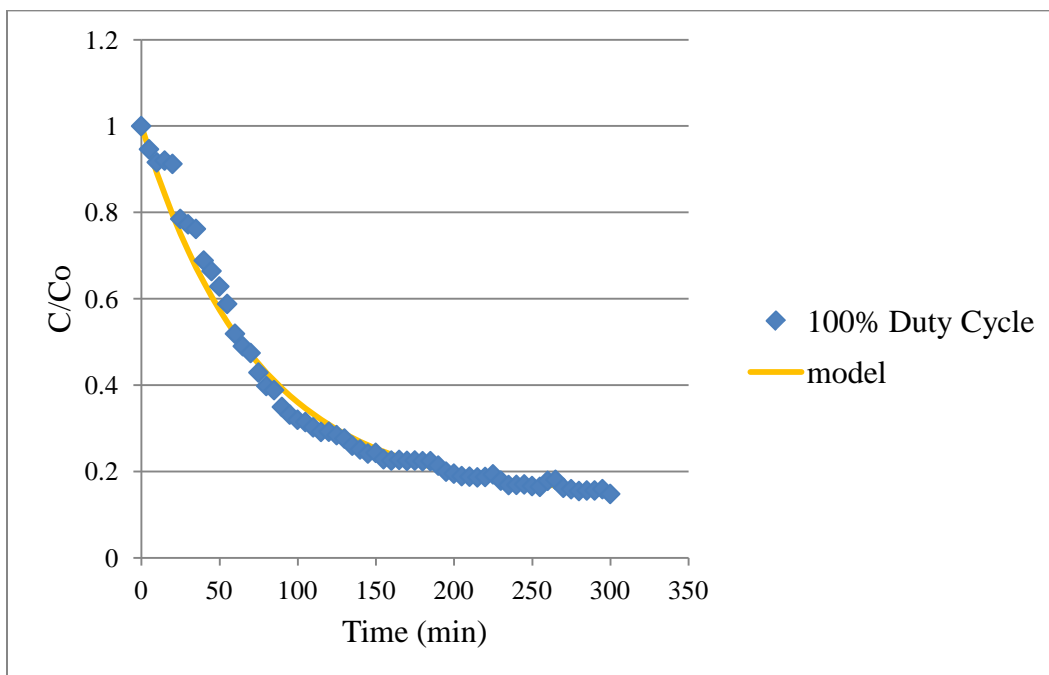


Figure 36 - 2nd Test Cycle, 100% Duty Cycle, at 0.7 ml Flow Rate, $k_s = 0.01181$, Model-to-Data $R^2 = 0.99$

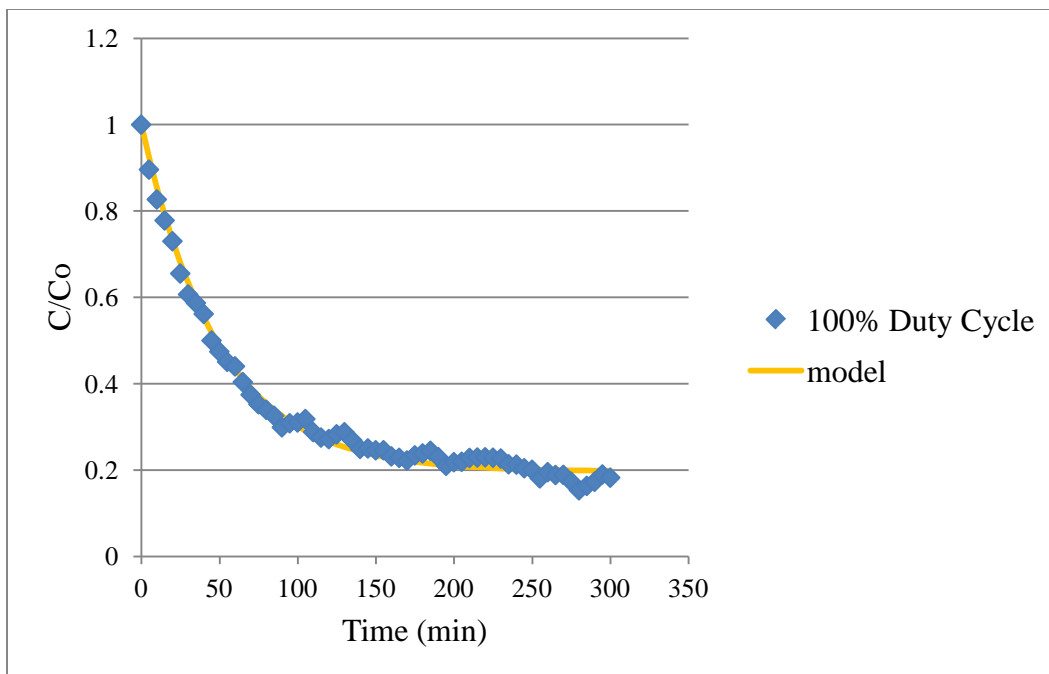


Figure 37 - 1st Test Cycle, 100% Duty Cycle, at 1.4 ml Flow Rate, $k_s = 0.01638$, Model-to-Data $R^2 = 0.99$

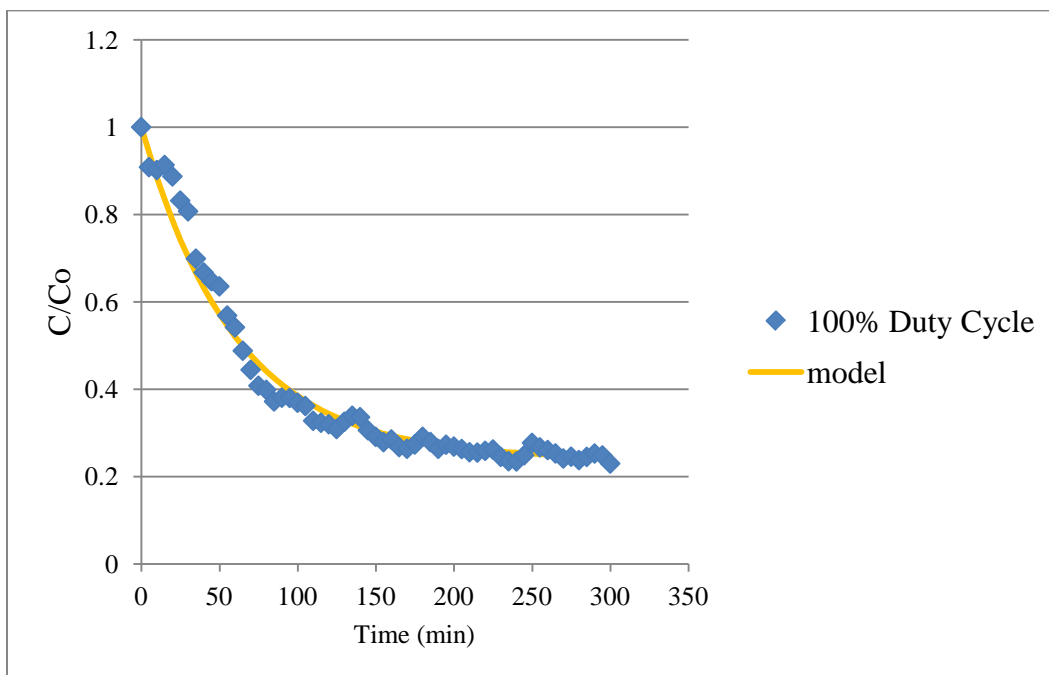


Figure 38 - 2nd Test Cycle, 100% Duty Cycle, at 1.4 ml Flow Rate, $k_s = 0.01264$, Model-to-Data $R^2 = 0.98$

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14. ABSTRACT Water contamination can result from terrorist acts, industrial accidents, or natural phenomena. Advanced Oxidation Processes (AOPs) represent a potentially useful method for water decontamination. This research explored the application of Brilliant Blue FCF as a witness dye in an Advanced Oxidation Process (AOP) employing Ultra-Violet (UV) Light Emitting Diodes (LEDs) with peroxide (H ₂ O ₂). In addition to exploring the attributes of Brilliant Blue FCF within this application, this research employed this dye to evaluate the effect of varied UV LED duty cycles (pulsing) on the reaction rates of a UV/H ₂ O ₂ AOP. Experiments performed using Brilliant Blue FCF indicated that it performed suitably as a witness dye with improved characteristics as compared to methylene blue. Further, the experiments indicated that when the LEDs were driven at lower duty cycles (e.g., 10 and 5%) they were 165% to 200% more efficient at driving the UV/H ₂ O ₂ AOP than they were when driven continuously (e.g., a duty cycle of 100%).					
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